JOURNAL OF

# CHEMICAL EDUCATION

VOLUME 30 April 1953 NUMBER 4

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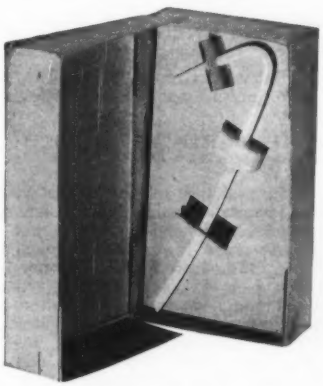

9823-F, Fig. 2.
Showing method of packaging Fittings.

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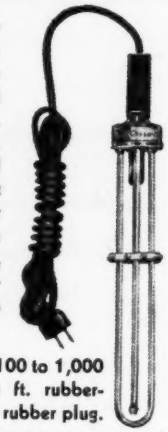

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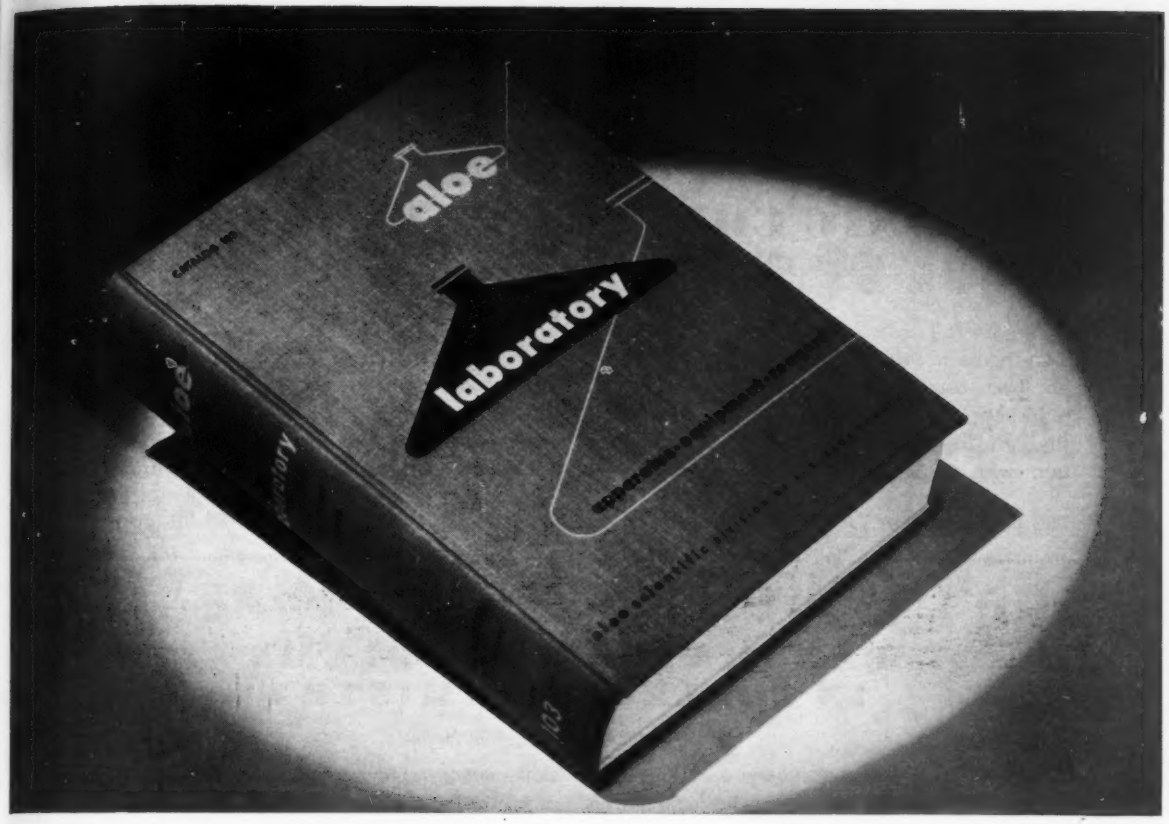


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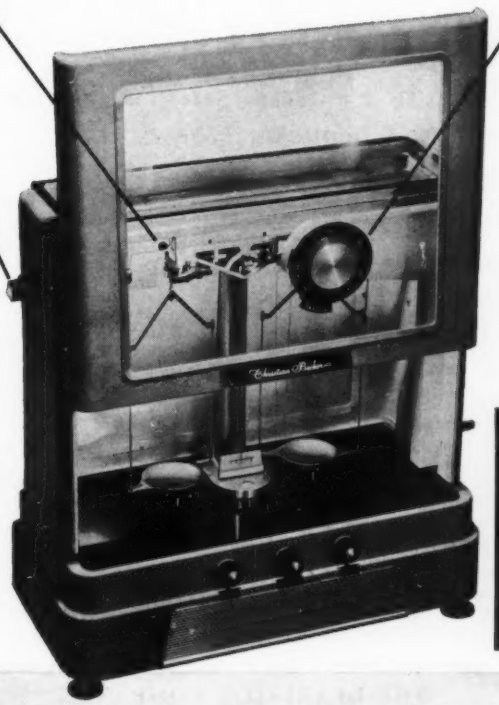

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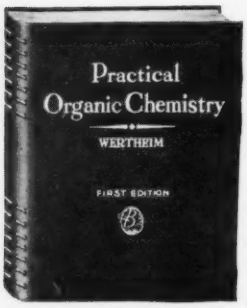


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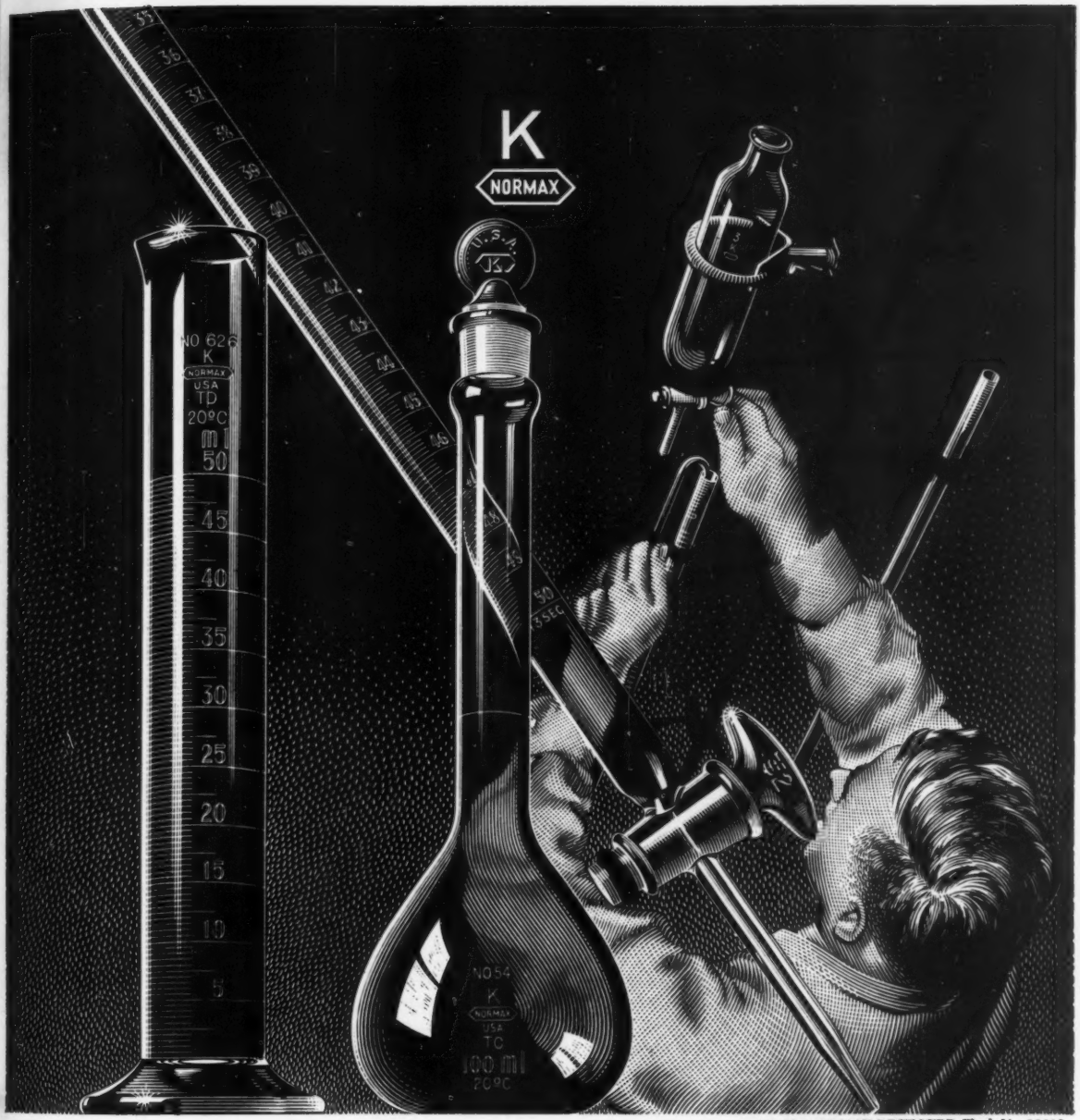


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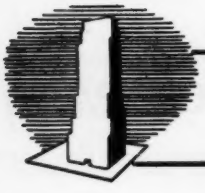

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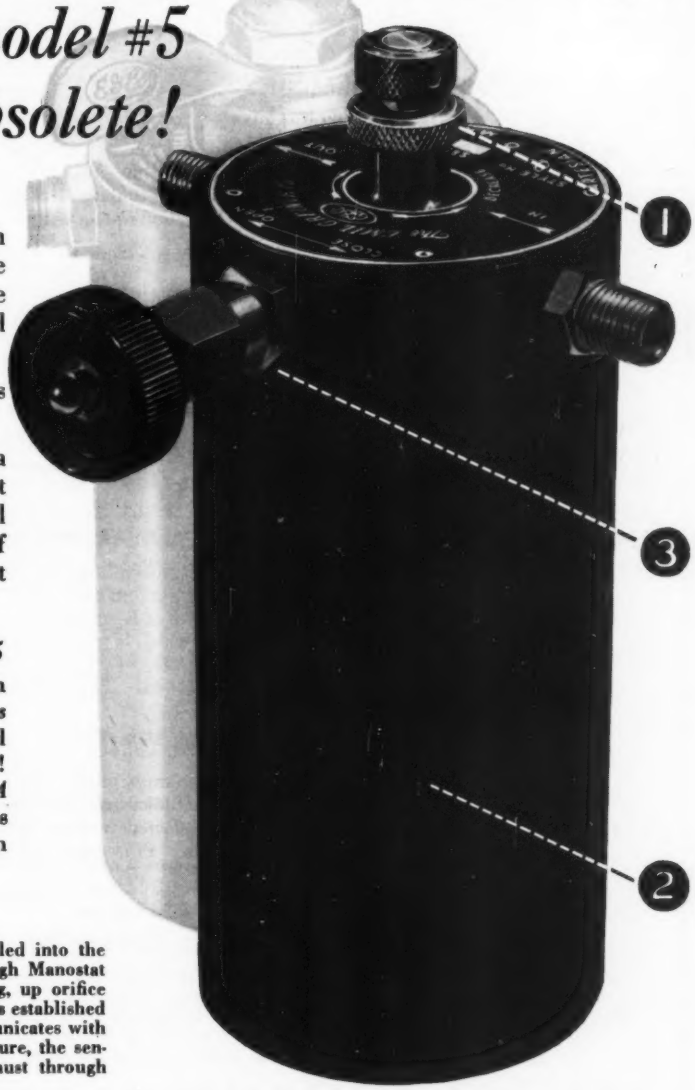


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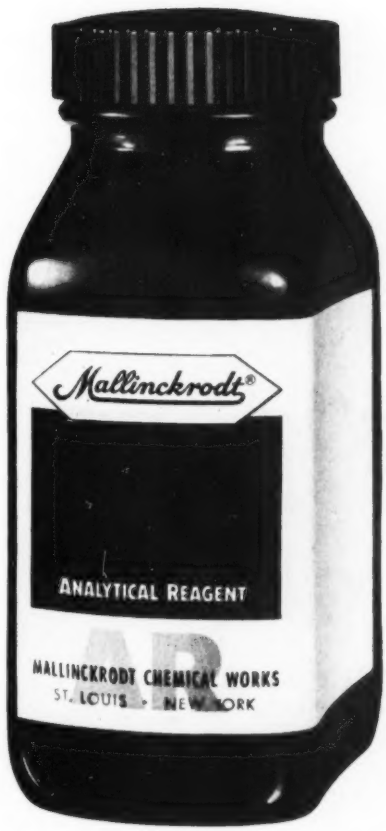


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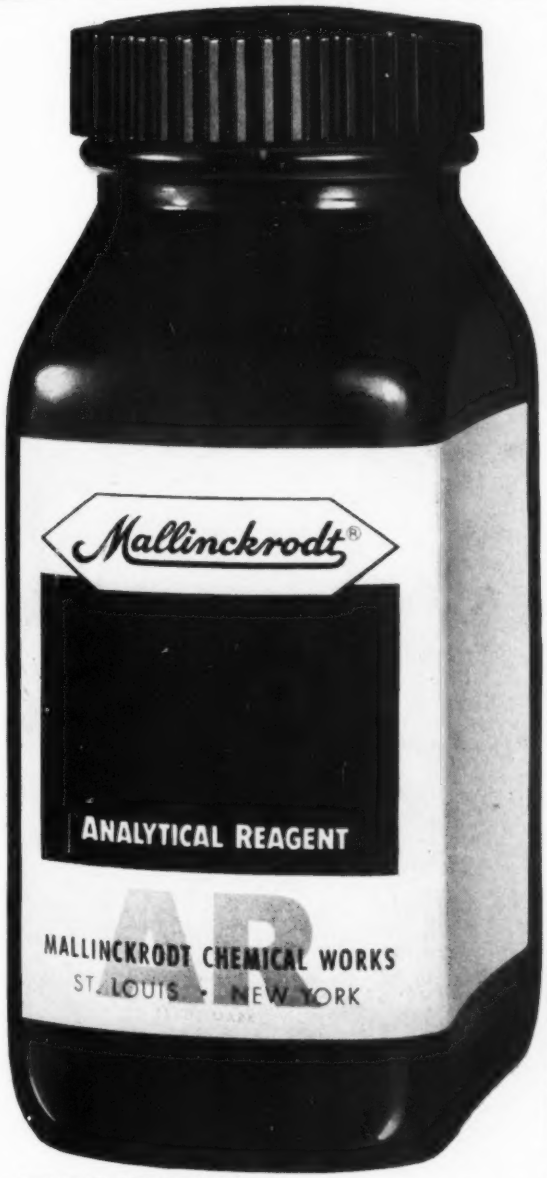


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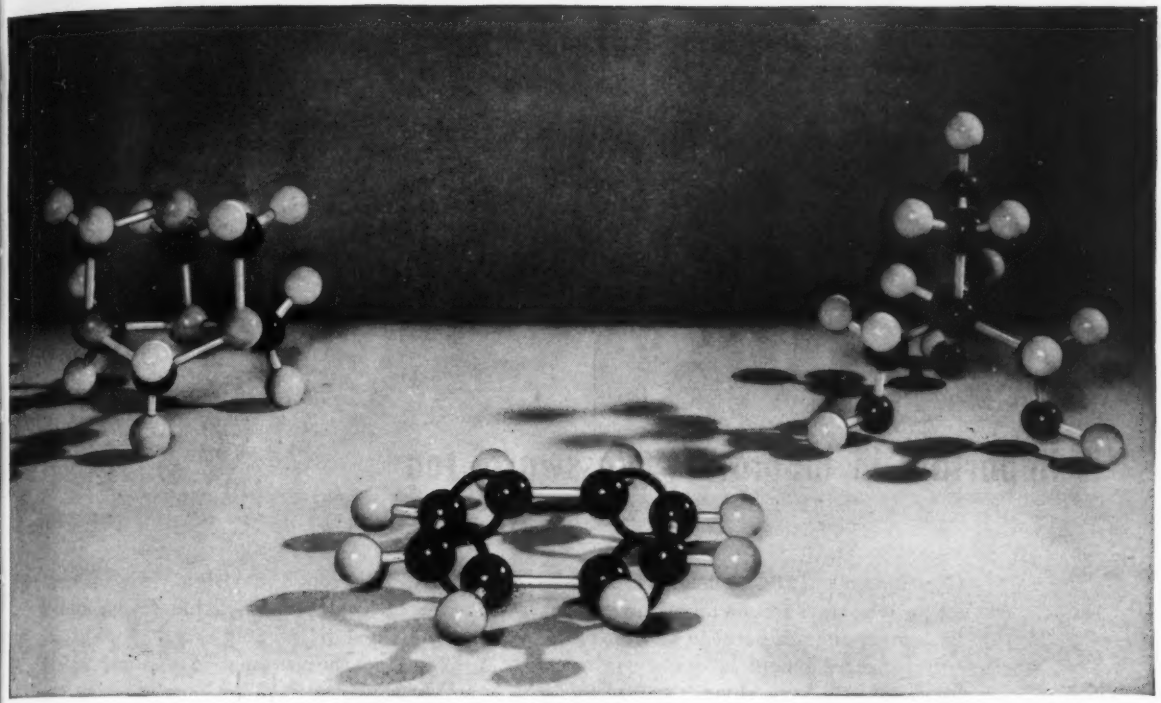

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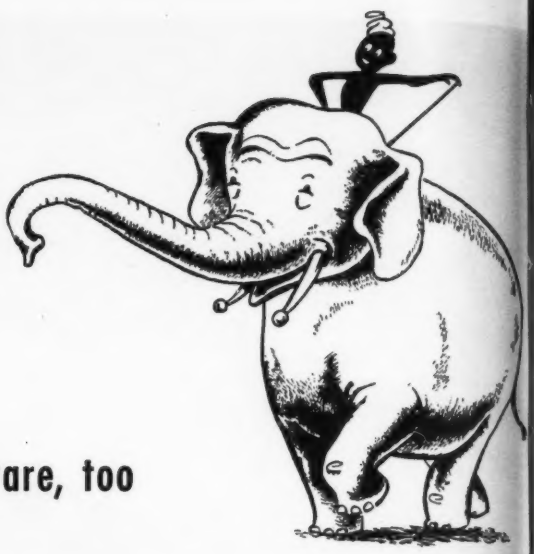

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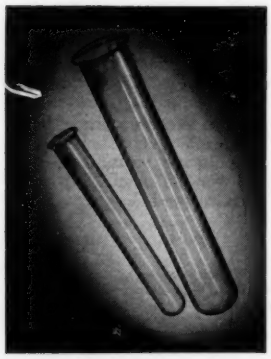

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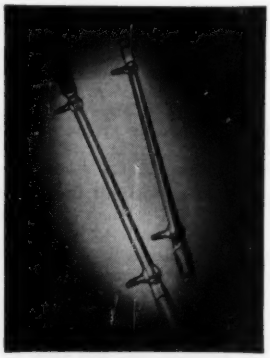

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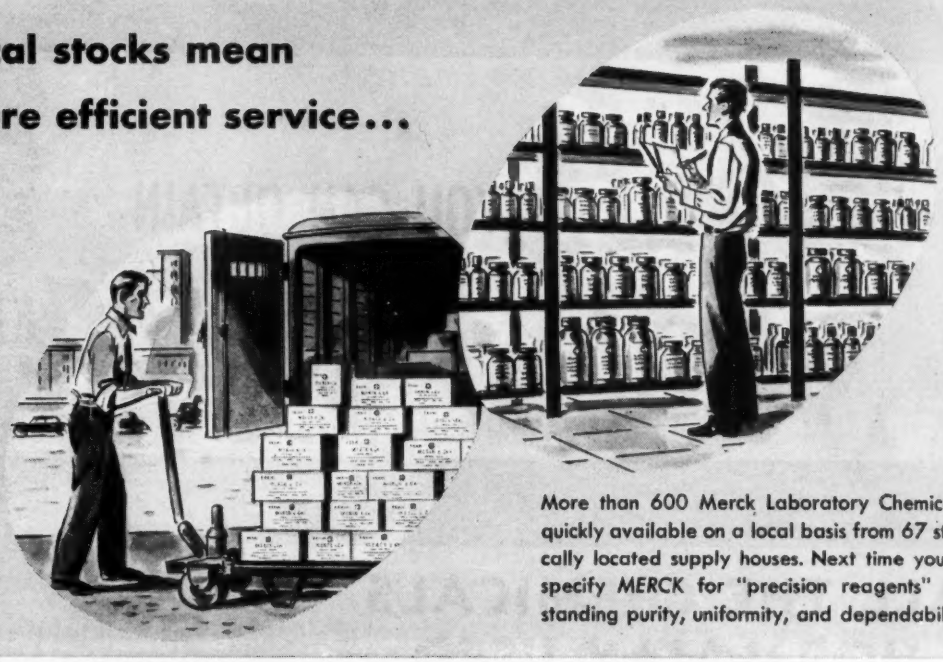

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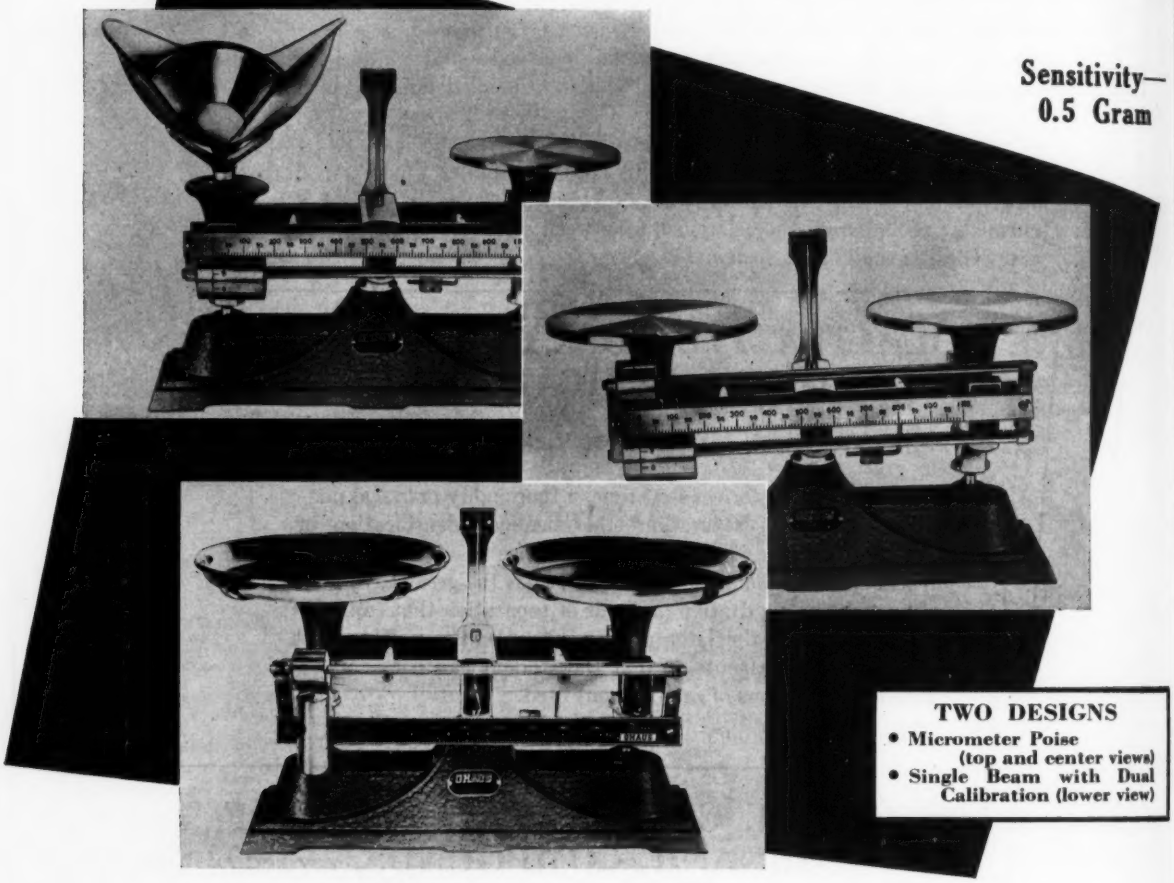


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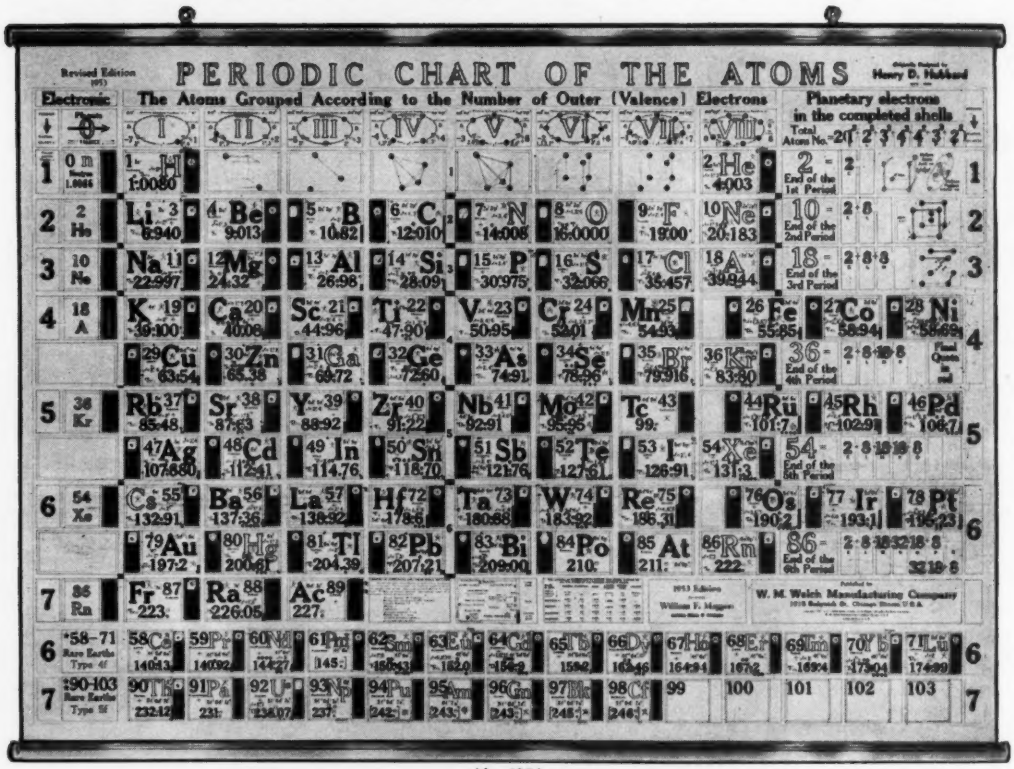


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# Editor's Outlook

THE question of the relation of the secondary-school teacher to the American Chemical Society has often been raised. Should the high school teacher be expected to join the Society, and if so, what advantages can he expect to get from his membership?

This is a hard question to answer; the cold fact, of course, is that relatively few such teachers have joined. This must indicate a lack of any very strong or widespread professional interest in their major subject. It is unusual to find a high-school teacher of chemistry with the professional drive and fortitude necessary to survive membership in the Society. On the other hand, it is just about as rare to find a member of the Society with any real interest in the problems of teaching young boys and girls—which is the real job of the high-school chemistry teacher.

This is not meant as an invidious comparison between anyone and anyone else; you just cannot compare a rose and a racehorse. Teaching chemistry in the high school is more intimately a part of teaching in the high school than it is a part of the profession of chemistry.

Consequently, I have always felt that the ideal organization for the high-school teacher is one like the New England Association of Chemistry Teachers, made up of teachers of chemistry in both secondary school and college but who are all interested fundamentally in the same kind of problems. This is about the only organization I have ever known in which teachers of both these groups have been able to meet on common ground.

But now it seems that high-school teachers are beginning to lose out even in such an organization as this. A report in a recent NEACT *News Letter* indicates that secondary-school teachers now compose only about half the Association's membership. In northeastern Massachusetts, where there are 260 secondary schools, only 58 of them have members in the Association; in New Hampshire, with 82 secondary schools, only 14. It goes on to say, however, that figures for secondary-school teachers in the other science-teacher organizations in New England are worse than those in the NEACT. If this is true in New England, generally supposed to be the conservative stronghold of education, the situation is doubtless much more extreme in other parts of the country.

"There is evidence, thus, of a lack of interest on the part of the secondary school teacher in the science that he is supposed to be teaching. This lack of interest may be a contributing cause to the decreased enrollment of students in science courses. If so, what can be done about reversing the trend?"

The conclusion about failing student interest may not be true, of course; mistaken vocational guidance and other propaganda may be much more important causes. Nevertheless, here are some facts which must be reckoned with. In the face of dwindling scientific man-power we are all of a sudden becoming conscious of the high-school teacher. But we must understand his problems and the forces under which he works before we can expect help from him. What is happening to science in the secondary school?—particularly what is happening to chemistry as a specialized science? Few of our professional chemists know very much about such matters—they only talk as though they do.

# SYNTHETIC FIBERS

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THE path of progress in any line of human endeavor is never a smooth one. Occasional periods of epoch-making advances are interspersed among less interesting periods of painstaking progress. Fortunate are those who are privileged to live in a period of flux when the application of principles discovered in another field enables them to participate in one of the forward surges of history. Such is the lot of scientists now engaged in the synthesis and development of new fibers, for today the textile industry is being revolutionized by application of the principles of modern organic and physical chemistry to the problems of fiber synthesis.

Once before, during the eighteenth century, the textile industry went through a similar revolution. Until that time, spinning and weaving operations were handicraft arts, evolved through centuries of trial and error, and handed down from parent to offspring. Then came the impact of a series of advances in mechanical science. In 1733 John Kay invented the flying shuttle for weaving and was rewarded by the burning of his home and machines by irate weavers who feared for the security of their jobs. During the second half of that century James Hargreaves invented the spinning jenny, James Watt adapted the steam engine to provide rotary motion, Richard Awkwright powered a roller spinning frame with water power, Samuel Crompton invented the spinning mule, Edmund Cartwright developed the first power loom, and Eli Whitney invented the cotton gin. Conventional ring and traveler twisting was invented by Thorpe, an American, in 1828 and cap-spinning by Danforth, another American, in 1829. These developments and accompanying improvements caused the British textile industry to expand at a phenomenal rate. Thus its consumption of cotton increased from something of the order of four million pounds in 1764 to something like 300 million pounds in 1833.

## CELLULOSIC FIBERS

Attempts were made to form synthetic fibers long before the sciences of organic and physical chemistry were well enough developed to be of any real assistance. Thus as early as 1855, Audemars, a Frenchman, drew out threads from a pool of nitrocellulose solution, solidified them in air, and wound them onto a spool. Several years later Azanam, another Frenchman, spun a solution of natural silk through jets of various sizes and thus pioneered the extrusion method of filament formation. About 1885 Swan in England and de Chardonnet in France perfected methods for spinning nitrocellulose fibers and subsequently denitrating them to the point where the fiber could be used in textiles. But this did not establish the rayon industry, for no rayon is made by the nitrocellulose process today. In 1892 Cross and Bevan learned how to prepare cellulose xanthate from alkali cellulose and carbon bisulfide; but without the assistance of modern fiber science it required a long list of inventors and another 20 years (until about 1911) to overcome the chief difficulties with the process for rayon manufacture. It was not until about 1930 that the industry made a product comparing at all favorably with today's yarn.

The second synthetic fiber to receive large-scale acceptance was acetate fiber, which was developed by the Dreyfus brothers in England after the first world war. These brothers had just placed in operation a large plant for the manufacture of cellulose acetate dope for airplane wings when they were faced with the sudden collapse of their principal market. Under the stimulus of this crisis they set out to develop a process for converting the dope to yarn. A year later they began offering samples of yarn to the trade, only to find it rejected emphatically because it could not be handled on ordinary textile machines or dyed with available dyes. Accordingly, they perfected fabricating and dyeing techniques, barely in time to preserve for them financial control of their enterprise. In so doing, they may have set a record for the speed with which a process for the manufacture of a new fiber was developed.

The success of these cellulosic fibers may well be considered but preliminary rumblings which foretold major events yet to occur in the fiber field. These could not take place until scientists had mastered the problems involved in synthesizing fibers from nonpolymeric raw materials. Yet, as we shall see, these cellulosics had a large impact upon many sectors of the textile industry.

The first cellulosic fibers were spun as continuous filaments like silk. As a result, they were dubbed "artificial silk." This was a mistake for they had neither the strength nor the elasticity of silk. However, from the very first, rayon fabrics had an aesthetic appeal approaching that of silk and far superior to that of cotton fabrics for intimate apparel. They offered variety to an industry which thrives on something new. During the 1920's a tremendous market opened up for rayon in the underwear and dress field based squarely upon aesthetic appeal. This appeal was enhanced by the spinning of yarns with very fine filaments, by the discovery of ways and means to control luster at any desired level, and by improvements of dyeing uniformity. The appearance of acetate pro-

vided a yarn with an even more luxurious feel than that of rayon. It made possible the development of a wide variety of crepes by weaving fabrics using an acetate warp and a highly twisted rayon filling, or by weaving the fabric from yarns made up of combinations of acetate and rayon filaments.

During the 1930's rayon and acetate invaded the staple-fiber field as well as the continuous-filament field. Again they capitalized upon aesthetic properties. For summer wear, in particular, very comfortable spun fabrics were produced. Those made with a high rayon content suffered from poor wrinkle-resistance, and to improve this the trade worked out crease-resistant finishes based on urea-formaldehyde or melamine-formaldehyde resins. Acetate staple, on the other hand gave better wrinkle-resistance and did not require treatment. The use of these staples is still expanding, particularly in the field of men's summer suitings, where they are reasonable in price and very comfortable.

During this same period fiber scientists, working with the assistance of newly discovered physical chemical techniques, learned how to increase the strength and toughness of rayon to the point where tires could be made with rayon cords. Before long these tires were giving more economical performance than tires made with cotton cords. During World War II large segments of rayon capacity were converted to the production of tire cord yarns.

Thus within certain sectors of the textile industry rayon and acetate have already worked a revolution. In terms of fiber consumption, the story is graphically depicted in Figure 1. The acceptance of rayon and acetate has been based mainly upon attractive aesthetic properties and reasonable durabilty. Descending, nonfluctuating prices have catalyzed acceptance. These fibers have made American women the best-dressed women in the world. For the first time in history the average (American) woman has been able to afford a variety of highly attractive dresses and an assortment of lingerie. The average woman in the United States is now said to own about six "party" dresses—"party" as distinct from house dresses. Prior to the advent of these fibers there were very few women with such a wardrobe. Rayon tire cords were first used primarily in truck and bus tires where service conditions were particularly severe. During recent years the use of rayon yarns in tires has been limited only by the availability of rayon productive facilities.

## FIBER SYNTHESIS

Scientists were seriously handicapped in their efforts at fiber synthesis as long as they had to depend upon nature to supply the polymers. This roadblock to progress was surmounted largely through the researches of Wallace Carothers and his associates in the Chemical Department at the Experimental Station of the du Pont Company in Wilmington, Delaware. In the late 1920's it became apparent to C. M. A. Stine, who headed the Chemical Department of du Pont, that the pace of industrial progress could be accelerated if industry were to supplement the fundamental research of the universities with fundamental research of its own conducted in carefully chosen areas of science where there existed an industrial need for basic knowledge. For example, at that time there was great debate as to the chemical structure of natural substances which we now class as polymers—that is, of cellulose, starch, rubber, silk, etc. Methods for the synthesis of high polymers were notably lacking.

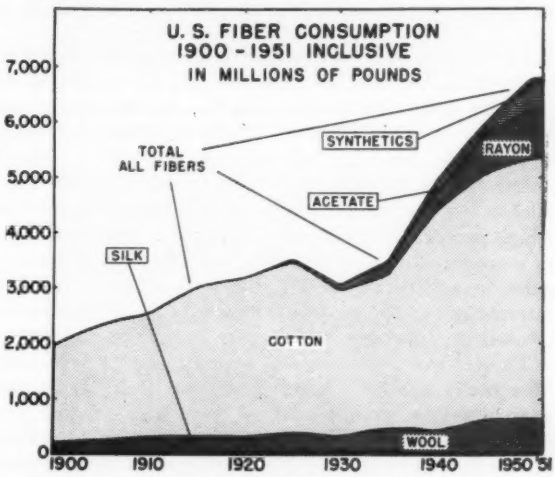


Figure 1

The data in this chart are presented cumulatively, so that the top line represents the total consumption for all fibers. To estimate the consumption of a particular fiber at any one time, measure the space occupied by that fiber against the scale on the vertical axis.

Accordingly, Wallace Carothers, a young organic chemistry professor of unusual promise, was engaged to conduct fundamental synthetic studies in the field of high polymers.

The researches of Carothers and his associates[1] were phenomenally successful. In a few years they had developed methods which enabled them to synthesize long, chainlike molecules having properties of the type formerly found only in such natural polymers as cellulose, rubber, and silk. Their efforts opened up a whole new field of synthesis for the industrial organic chemists. From the host of polymers which these men put together in the laboratory, two were initially selected for commercial development—one was nylon, the other neoprene, a synthetic rubber.

In retrospect, the elements of fiber synthesis are not difficult to comprehend, for the fiber scientist follows a procedure quite analogous to that which has been used by man through the ages for the production of spun yarns (see Table 1). For example, for centuries man has selected naturally occurring fibers which

[1] MARK, H., AND G. S. WHITBY, Editors, "Collected Papers of Wallace Hume Carothers on High Polymeric Substances," Interscience Publishers, Inc., New York, 1940.

**TABLE 1**
**Fiber Synthesis-Spun Yarn Analogy**

| | *Spun yarns* | *Synthetic fibers* |
|---|---|---|
| (1) Raw material | Fibers of long length relative to diameter | Linear molecules of long length relative to diameter |
| (2) Orientation | Fibers carded to orient them parallel to yarn axis | Extruded filament stretched in solid or semi-solid state to orient molecules parallel to fiber axis |
| (3) Bonding forces | Twist and friction | Attraction of polar groups |

are of long length relative to their diameter, has oriented them parallel to the yarn axis by a carding or combing operation, and finally has bonded them together by twist and friction. Currently, the fiber chemist first synthesizes a linear polymer, one with very long length relative to its diameter, orients its molecules parallel to the fiber axis by one of a number of ways, all of which involve stretching of an extruded filament while in a solid or semisolid condition, and causes the molecules to adhere to one another by developing strong intermolecular forces between polar groups previously located at appropriate intervals along the molecules.

These three steps for the formation of a synthetic fiber really involve control of six important structural variables—the chain length of the linear polymer, its flexibility, the nature of the intermolecular forces operating between chains, the degree of orientation, the degree of crystallinity, and finally the morphology of the filament which deals with inhomogeneities within the filament.

## 66-NYLON

*Preparation.* Having taken this initial plunge into the complexities of fiber synthesis, let us consider in some detail nylon 66, the first fiber to be manufactured from nonpolymeric raw materials. This fiber was assigned the code number 66 because the polymer from which it is spun is polyhexamethylene adipamide formed from the 6-carbon diamine (hexamethylenediamine) and the 6-carbon acid (adipic).

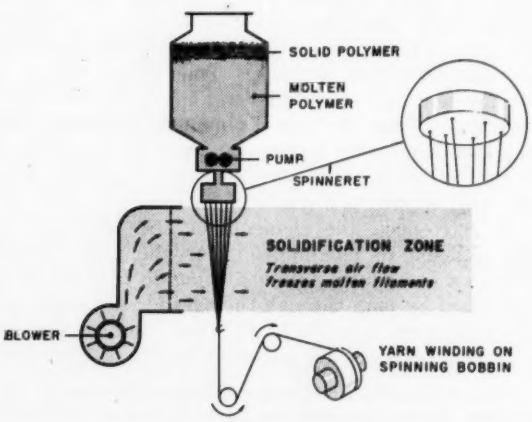


**Figure 2. Melt Spinning**

In manufacturing 66 polymer a salt is first formed from equimolar quantities of the acid and diamine. A molecule of water is then split from each of the salt links by heating to super-atmospheric pressures in water solution and bleeding off the water vapor. Molecular weight can be controlled by the addition of a suitable amount of monofunctional acid or amine, or by controlling the extent of water removal during polymer preparation.

Polymerization can be carried out in batch equipment and the polymer isolated by casting a ribbon of the melt into water and cutting into flake form. In such event, spinning is carried out in a separate operation (Figure 2), comprising the steps of (1) melting of the flake, (2) pumping and filtration of the melt, (3) extrusion of the filaments through spinnerets into a freezing zone where the flow of air is very carefully controlled, and finally winding into a package at rates of the order of 40 miles per hour. The problems encountered in polymerization are largely chemical engineering in nature, whereas those connected with spinning involve mechanical engineering of a high order. Pumps and spinnerets are manufactured and maintained by procedures which rival those of the watchmaker. Control of the freezing of the filaments and winding of large bobbins of yarns at high speeds without damage to the delicate yarn posed novel mechanical problems which had to be solved before commercially acceptable yarn could be produced. Polymerization may also be integrated with the spinning step, thereby eliminating the preparation and melting of flake polymer. In such event, the chemical engineering and control problems associated with polymerization become much more complex.

Nylon filaments on the spin-bobbin are made up of an unoriented mass of linear molecules kinked in random shapes by the thermal motion of their component segments while in the molten condition. Figure 3*a* shows an X-ray diagram of such a filament taken by passing a beam of X-rays through a bundle of filaments perpendicular to their common axis and registering the diffracted X-rays on a photographic plate located behind the filaments. This pattern takes the form of two concentric diffuse rings. The presence of two rings (rather than a single, more diffuse ring) shows that over short intervals of length segments of adjacent molecules have formed crystallites. The absence of any appreciable variation in the intensity of these rings along their circumference is proof that these crystallites have no preferred orientation with respect to the fiber axis. Figure 3*b* is a similar X-ray diagram of a nylon fiber after it has been stretched to approximately four times its initial length. The two concentric circles have now broken into two pairs of concentric arcs, thereby demonstrating a high degree of orientation parallel to the fiber axis. Study of the distribution of intensity over the arcs in a radial direction indicates that further crystallization has taken

place. Crystallization is favored still more by drawing at an elevated temperature. The molecules are now bonded in an oriented position and a most remarkable change has been wrought in the physical properties of the filaments. Strength has been increased 4- to 6-fold and the filaments have excellent elasticity. This is shown graphically in Figure 4 and the manner in which the properties change with draw ratio is shown in Table 2.

**TABLE 2**
**Change in Physical Properties with Change in Draw Ratio**

| *Draw ratio* | *Temperature of drawing* | *Tenacity* | *Elongation* | *Moisture sorption 78°F. 72% r.h.*[a] |
|---|---|---|---|---|
| 2.51 | Cold | 2.2 g/d[b] | 160%[c] | 4.67% |
| 3.45 | Cold | 3.1 | 89 | 4.52 |
| 4.47 | Cold | 4.6 | 50 | 4.29 |
| 5.01 | Cold | 5.8 | 36 | 3.90 |
| 5.38 | Cold | 6.6 | 22 | 3.75 |
| 6.07 | Hot | 8.2 | 21 | 3.54 |

[a] Relative humidity.
[b] Grams per denier. Denier is a measure of weight per unit length, *i. e.*, the weight in grams of 9000 meters.
[c] Suter Tester.

In many ways this cold drawing operation is typical of the synthetic fiber industry, for in this one step, after the stage has been set by synthesis of molecules of precisely the right chemical structure and dimensions, and by extruding a mass of these molecules into filament form and conditioning them to adjust intermolecular forces to the desired level, a purely mechanical operation completely reorganizes the molecular arrangement and occasions a phenomenal improvement in physical properties. More complex examples could be cited, but none which are any more dramatic.

**TABLE 3**

| | *Nylon* | *Silk* | *Textile rayon* | *Tire cord rayon* |
|---|---|---|---|---|
| Tenacity (g/d) | 4.8–7.2 | 4.0 | 1.6–2.5 | 2.6–3.9 |
| Elongation (%) | 24–18 | 14 | 15.5–17.5 | 8–10 |
| Elastic modulus (g/d) | 45 | 115 | 83 | 84 |
| Recovery from 10% stretch | 91% | 47% | 24% | Breaks |
| Abrasion-resistance (yarn) | 15,600 | 2,485 | 1,575 | 45 |

*Properties.* Nylon possesses an outstanding combination of high strength, elasticity, toughness, and abrasion-resistance, as shown in Table 3. It is believed that these properties stem directly from the length of the chain (of the order of 100 monomer units), the great flexibility of the polymer chain, the relatively high polymethylene content of the chain, the strength of the forces operating between the amide groups, and from steric factors which are favorable to efficient operation of these forces. The flexibility of the chain derived

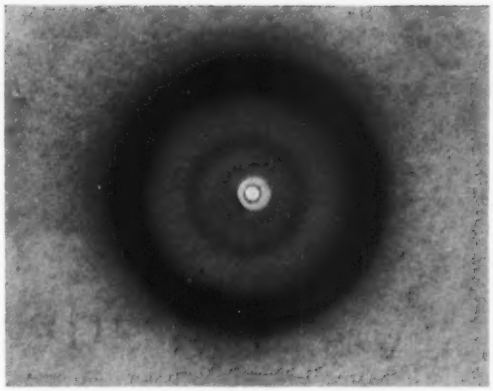

Figure 3a. X-ray Diffraction Photograph of Freshly Spun, Undrawn, and Consequently Unoriented Nylon

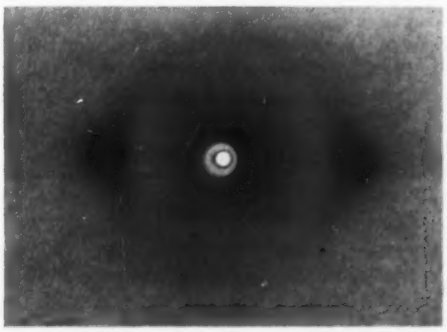

Figure 3b. X-ray Diffraction Photograph of Oriented Nylon That Has Been Drawn to About Four Times Its Original Length

from its high polymethylene content serves to give the fiber a relatively low elastic modulus (ease of stretch), regardless of the degree of orientation or the degree of crystallinity. Hydrogen bonds formed between carbonyl oxygens on one chain and imino hydrogens on adjacent chains provide points of very strong binding along the chain. The structure of 66 polymer is such that when the chains are fully extended each amide group can bond in two directions (Figure 5). The length of this bond is about 2.8Å., indicating that as hydrogen bonds go this is a fairly strong bond. Something of the order of 5,000 to 10,000 calories is

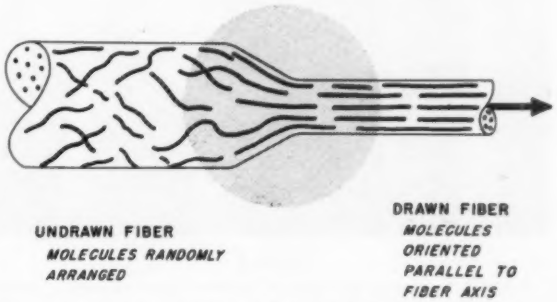


Figure 4. Alignment of Molecules by Stretching Fiber

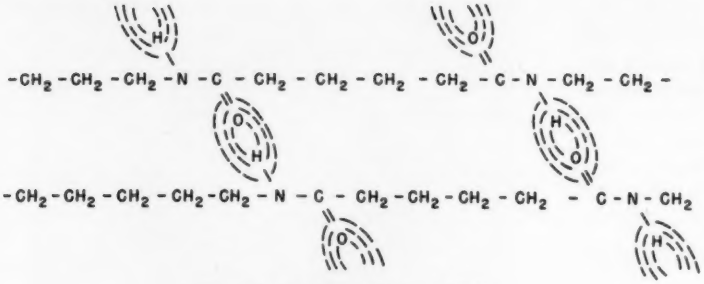

Figure 5. Crystalline Lattice of Nylon

probably required to break it.[2] The strength of these bonds and the regularity of their location along the chain which contributes to close packing and crystallization are responsible for the high melting point of nylon 66. They contribute to the strength of the fiber and to its high elastic recovery. Toughness seems to result from the combination of low elastic modulus (and high elongation), which favors spreading of the load to all parts of the fiber or fabric, and high strength, which prevents rupture of the structure.

The extraordinary strength and toughness of nylon are capitalized upon in the 15-denier ladies' hose which are so popular today. These are knit from a single filament of nylon! They were designed as party hose, to be the ultimate in sheerness, but now, much to everyone's surprise, they outsell all other hose for everyday wear by the office girls of the U. S. A. They are so sheer that they contain only about three-fourths of the weight of yarn that was formerly used in silk party hose which were considered good for only one evening's wear. To be sure, they do not wear as well as the 40-denier stockings which were so popular prior to World War II, but they give surprising wear for the small amount of nylon which they contain.

A unique property stems from the high bonding energy of the amide groups. When nylon yarns are exposed to hot water, steam, or high temperatures for the first time, the fiber takes on a practically permanent set. X-ray pictures show this to be a crystallization process. The crystal forces developed in this manner are not relaxed by exposure to moisture or even to heat unless much more drastic conditions are employed than were used in the initial setting.

[2] MARK, H., AND A. V. TABOLSKY, "Physical Chemistry of High Polymeric Systems," Interscience Publishers, Inc., New York, 1950, Vol. II, p. 150.

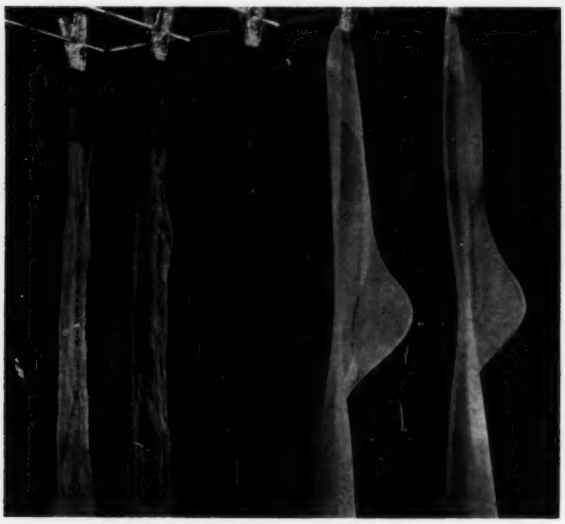

Figure 6

Wrinkled stockings on left were not heat-set before being dyed. Stockings on right were put on a form, exposed to steam, and then were dyed, emerging wrinkle-free from the dye bath.

Figure 7. Permanently Pleated Negligee and Nightgown (manufactured with du Pont nylon by Vanity Fair)

This phenomenon was uncovered when the first attempts were made to dye nylon hose. Permanent wrinkles such as are shown in the stockings on the left in Figure 6 were set in the hose by the hot dye bath. The remedy for this difficulty was found to be to "set" the hose in steam while they were stretched over a form *prior to dyeing* (Figure 6, right stockings). Thus set in the unwrinkled condition, they did not develop permanent wrinkles in the subsequent dyeing operation.

Perhaps a more dramatic example of the exploita-

tion of this effect is in the manufacture of permanently pleated garments, such as the negligee and nightgown shown in Figure 7. Laboratory tests have shown the pleats in garments like these to be permanent to some 80 washings, at which time the test was discontinued. These garments created a sensation in the trade. The same property is basic to the phenomenal success currently enjoyed by garments made from nylon tricot fabric. Such garments are dimensionally stable because of the heat-setting properties of nylon, whereas similar garments knit from rayon would not retain their shape or dimensions through laundering.

### 6-NYLON

Shortly after du Pont had its 66 venture under way, the I. G. Farbenindustrie in Germany chose to commercialize a nylon derived from caprolactam and given the trademark "Perlon." This type of nylon had been made earlier by du Pont from aminocaproic acid (see ref. 1).

Under the influence of a suitable catalyst (for example, aminocaproic acid or metallic sodium), the ring of caprolactam is opened and a linear polymer formed:

$$n\left(\begin{array}{l}CH_2CH_2CH_2CH_2CH_2CO\\ \quad\quad\quad\

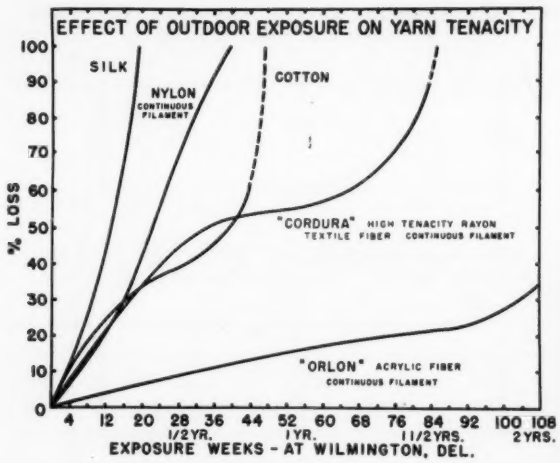


**Figure 10**

Exposure tests show "Orlon" acrylic fiber retains over 70 per cent of its original tenacity after about two years' exposure. The dotted lines on cotton and "Cordura" high tenacity rayon yarn indicate some uncertainty in the latter test phases for these two fibers.

atmosphere or wet-spun into a coagulating bath. Regardless of the method of spinning, polyacrylonitrile fibers always seem to be crystalline in nature, never amorphous. Perhaps because of this crystalline nature it is always necessary to heat or to swell the fiber if one wishes to orient it by stretching. In the absence of heat the unoriented fiber merely breaks when a stretching force is applied.

*Properties of "Orlon."* One of the most spectacular properties of this fiber is excellent light-resistance. As a result, some persons have referred to it as "the outdoor fiber" (Figure 10). Fully oriented, filament "Orlon" has substantially better light-resistance than other commercial fibers. Some dyes, for example certain basic colors, which have poor light-fastness on other fibers have good light-fastness on "Orlon." If more than a minor proportion of other vinyl monomer is copolymerized with acrylonitrile in forming the polymer, or if the fiber is only partially oriented and is less dense than normal crystalline polyacrylonitrile, as is the case with "Orlon" staple, then this exceptional light-resistance is lost.

Filament "Orlon" is noted for its silk-like feel which is believed to result from a similarity in the stress-strain curves of the two fibers (Figure 11) over the first 5 to 10 per cent of stretch (see later discussion of the feel of wool-like fibers) and the fact that both fibers have a rough surface giving their fabrics a scroop or rustle. Figure 12 shows a wedding dress fashioned by Murray Hamburger which uses the luxurious aesthetic properties of "Orlon" to advantage.

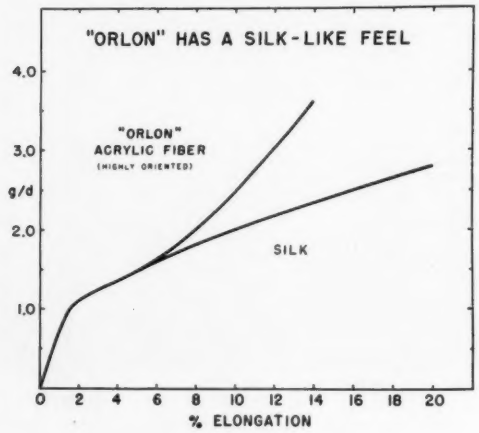


**Figure 11**

**Figure 12. Bridal Gown of "Orlon" Acrylic Fiber Designed by Murray Hamburger & Co.**

In either filament or staple form, "Orlon" acrylic fiber has high bulking and covering power in fabrics. Since the bonding forces operating between the polymer chains are insensitive to moisture, "Orlon" retains its bulk under service conditions even when wet with water. Consequently it is a warm fiber and is used to advantage in such garments as the Washable Topper Coat shown in Figure 13. Pile fabrics, such as this coat, and knitted fabrics of "Orlon," like their nylon counterparts, have outstanding crease- or crush-resistance and dimensional stability. In tightly constructed, woven fabrics, the frictional properties of "Orlon" work against recovery of the fabric from wrinkling and consequently a little ironing is usually required, but wrinkles are removed with extreme ease.

## POLYESTER FIBERS

The researches of Carothers and his associates began with polyesters and uncovered many fiber-forming polymers, but their search for structures with high melting points and hydrolytic stability led them into the field of polyamides and resulted in the development of nylon. During the war period, two English scientists, Whinfield and Dickson[3] uncovered the excellent fiber-forming characteristics, high melting point, and hydrolytic stability of polyethylene terephthalate during the course of an investigation of the effect of molecular symmetry on the microcrystallinity of polymers. From the vantage point of hind-sight it now seems probable that by incorporating benzene nuclei these inventors stiffened the chain and added to cohesive forces as well; by using the para derivative they achieved excellent fit between adjacent chains, thus favoring crystallization and efficient operation of intermolecular forces (Figure 14); and finally by using ester groups instead of amide groups they kept the melting point of the polymer within bounds (250° C.). Had they prepared the amide, its melting point would have been much higher and the polymer would have been most intractable. Hill and Walker[4] have attributed the excellent hydrolytic stability of this polyester to its low water absorption and high crystallinity. Du Pont purchased the U. S. patent to polyethylene terephthalate and has now developed a fiber from it, given the trademark "Dacron." In Britain, the Imperial Chemical Industries is developing a similar fiber under the trademark "Terylene."

[3] WHINFIELD, J. R., *Nature*, **158**, 930 (1946).
[4] HILL, R., AND E. E. WALKER, *J. Polymer Sci.*, **3**, 609 (1948).

**Figure 13. Topper Coat Made of "Orlon" Acrylic Fiber**

Coming out of the electric dryer ready to wear, and retaining all its original fluffy beauty, this fleece coat of 100 per cent "Orlon" acrylic fiber was machine washed and dried in a period of only about 45 minutes.
Garment manufacturer: Leeds, Ltd.
Fabric manufacturer: Princeton Knitting Mills

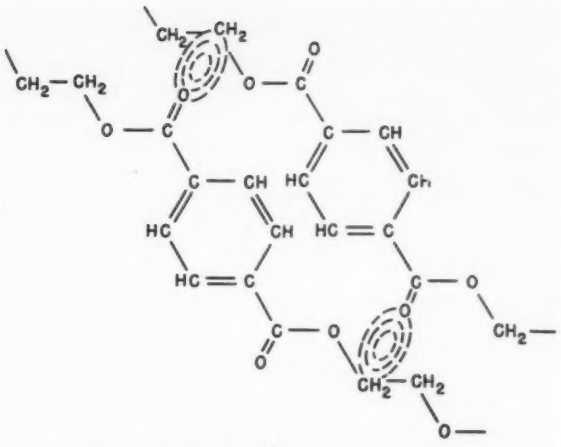

**Figure 14. Crystalline Lattice of "Dacron" Polyester Fiber**

Polyethylene terephthalate polymer can be extruded and oriented by techniques having many points in common with those used with nylon. Fully oriented filaments are relatively stiff, stretch-resistant fibers, due most likely to the benzene rings in the polymer chain which greatly stiffen it. This fact is showed by the steep slope of the stress-strain curve for "Dacron" in Figure 15. Stretch-resistance of this type is useful in sewing threads and in fire hose, where "Dacron" makes up the pressure-resisting member of the hose. However, the most outstanding property of "Dacron" polyester fiber is its excellent crease-resistance in woven as well as knitted fabrics and under moist conditions as well as dry. This is believed to result from the

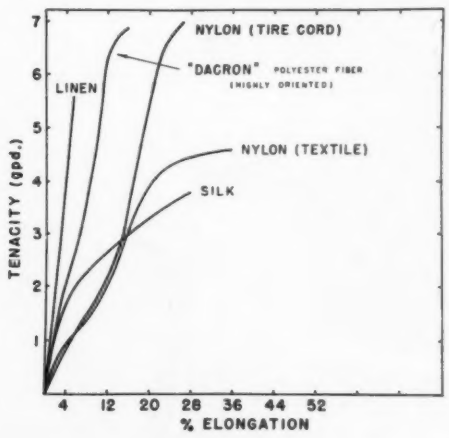


**Figure 15**

stiffness of the chain and the bonding forces between the chains which, like those in polyacrylonitrile fibers, are insensitive to moisture. These forces are believed to reside mainly in bonds formed between the carbonyl groups on one chain and methylene groups on adjacent chains. They seem to be a little stronger than those in the acrylic fibers but weaker than those in nylon. Thus pleats can be inserted with a "rayon" iron, but these pleats are a little harder to iron out again than are those formed in acrylic fiber fabrics. Garments made of "Dacron" absorb so little moisture that they dry even more rapidly than those made of nylon or "Orlon."

In Figure 16 is shown a model dressed in a blouse made of "Dacron" and pleated skirt made of 55% "Dacron" and 45% wool by Deering, Milliken and fashioned by Nathalie Nicoli of New York City. Both are shown after washing and no ironing.

## THE WOOL PROBLEM

For many years the functional properties of wool have stood out as prime objectives for fiber synthesis.

**Figure 16. Blouse Made of 100 Per Cent "Dacron" Polyester Fiber by The Kramer Company. Skirt Made by Nathalie Nicoli of a Fabric of 55 Per Cent "Dacron" and 45 Per Cent Wool (washed but not ironed)**

Superficial wool-like properties such as fuzziness and initial bulk can be built into yarns from all synthetic fibers by chopping them into short lengths (staple fiber), suitably crimping the fibers, and finally spinning them into yarn by procedures used for wool or cotton. Yarns prepared in this manner from rayon and acetate have been used with great success in women's wear and summer suitings, but they are deficient in liveliness and crease-resistance, particularly at high relative humidities, and tend to lose their bulk in service. Urea and melamine-formaldehyde finishes do much to minimize these defects. Rayon staple fabrics have a feel quite different from wool fabrics, though, for reasons which will be examined later, acetate staple fabrics approach the feel of wool more closely. When the new synthetics, nylon, "Orlon" acrylic fiber, and "Dacron" polyester fiber, made their appearance, an immediate attempt was made to tailor wool-like staple fibers from these polymers. As experiments progressed, one by one the principal functional properties of wool were equaled or excelled until now only the felting and fulling (shrinkage) properties of wool remain to be matched.

Nylon staple can be given an intense crimp which can be set in place by steaming. The resulting fiber spins to bulky yarns which give warm sweaters with good recovery properties. On the other hand, worsted fabrics made from this fiber feel quite unlike wool, and only when properly constructed and heat-set do they have good wrinkle-resistance. Once heat-set, it is no longer possible to iron pleats or creases into the fabric, nor is it possible to remove creases or pleats which were set in the fabric during the initial setting. The cross bonds in the nylon fiber are too strong to be thawed by the heat of the iron! Since nylon has many time the abrasion resistance of most other fibers, a major use for it is as a blending fiber to contribute strength and abrasion-resistance. Thus 15 per cent of nylon stable is frequently blended with wool in the spinning operation to permit the spinning of finer yarns and to improve the wear of fabrics.

The outstanding properties of "Orlon" acrylic staple fiber are its high bulk and cashmere-like feel. Like nylon, "Orlon" is not a particularly lively fiber (recovers lazily from stretch rather than rapidly) and its high surface friction works against its recovery from wrinkling by serving to anchor the fibers in the deformed state. Consequently, "Orlon" staple gives particularly good service in loose structures such as in knitted wear and in woolen system fabrics. When properly constructed such fabrics do not pill. Pilling is a defect sometimes observed during the wear of staple fabrics wherein small balls of fibers accumulate on the surface of the fabric. Many persons admire the luxurious softness of woolen system fabrics, but are more apt to buy worsted fabrics which are crisp and harsh in feel, in order to gain the additional wrinkle-resistance, crease-retention, freedom from bagging at the knees, and the additional durability generally associated with worsted suits. The blending of a substantial proportion of acrylic staples with wool now opens the way to prepare fabrics on the woolen system which will have the softness and warmth of 100 per cent wool fabrics, but rival worsted fabrics in their retention of neat appearance during wear and in their durability.

Since the bonding forces between polymer chains in "Orlon" are relatively weak, they are easily "thawed" by exposure to the temperature of an iron set to a rayon setting. The heat of the iron breaks the bonds between chains permitting the fibers and fabric to be deformed by the weight of the iron. Upon cooling, the bonds reform and the fibers and fabric are "locked" in the pressed condition. Unlike the bonding forces existing in wool or cellulosic fibers, the bonding forces in "Orlon" are not broken by moisture. Consequently pleats, permanent to washing, can be ironed into the fabric and removed again with the same iron. Figure 17 shows such a dress knitted from "Orlon" staple yarns, fashioned by Carolyn Schnurer of New York City. This photograph was taken after washing. Not only are the pleats stable to washing but likewise the dimensions of the garment.

The principal functional properties of wool are probably most difficult to match in tightly constructed, worsted fabrics. In these fabrics, "Dacron" polyester staple probably does the best job of matching the liveliness, wrinkle-resistance, and feel of wool. The situation with respect to the first two of these properties is summarized in Table 5. In making these evaluations, the rate of unfolding of a fabric from a bend around a sharp edge was followed with a photoelectric cell and taken as the measure of liveliness. Crease recovery was measured after holding the fabric in the creased state for five minutes.

**TABLE 5**

| *Fiber* | *Rate unfolding 65% r.h.*[a] | *Initial crease-recovery 65% r.h.* | *90% r.h.* |
|---|---|---|---|
| "Dacron" polyester | 62 cm./sec. | 83% | 81% |
| Wool | 69 | 78 | 66 |
| "Orlon" acrylic | 40 | 72 | 67 |
| Nylon | 39 | 66 | 66 |
| Acetate rayon (resin treated) | | 62 | 46 |

[a] Relative humidity.

These measurements were run on as nearly comparable tropical worsted fabrics as our Textile Research Division was able to construct; however, it must be admitted that valid comparisons of this type are exceedingly difficult to make. It is to be noted that the crease-recovery data taken at high relative humidities are particularly favorable to "Dacron" and "Orlon."

Wool fabrics have a unique feel or compliance quite different from that of other natural fibers. When deformed to a slight extent they feel *crisp;* when bent more sharply they feel *soft.* The crisp feel for small deformations is easy to match with any synthetic fiber by suitably adjusting filament diameter and elastic modulus, but when this is done one generally obtains a fabric which feels stiff and boardy when bent more sharply, rather than soft and compliant as do wool fabrics when similarly bent. Conversely, if the elastic modulus and filament diameter are adjusted to give fabrics which feel soft to a sharp bend, they do not feel crisp to a light touch.

**Figure 17. Jersey Dress Made of 100 Per Cent "Orlon" Acrylic Staple Fiber (after washing)**

Fabric manufacturer: Alamac Mills
Garment manufacturer: Carolyn Schnurer

There was a time when it was suspected by many that this unique feel of wool would never be closely matched except through the synthesis of fibers from alpha-amino-acid polymers. However, some of the members of our Pioneering Research Division took a mechanical approach to the problem (Figure 18).

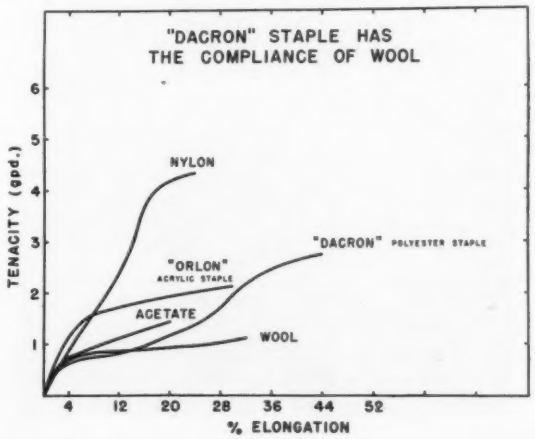


**Figure 18**

They[5] attributed the crisp yet soft feel of wool to a bend in the stress-strain curve which makes the fiber easier to stretch or bend the more you stretch or bend it. The critical range in elongations is between about 5 and 10 per cent. Such elongations seem to characterize the deformations occuring in fibers when a fabric is bent in service. When staple fibers were tailored from polyethylene terephthalate to duplicate the stress-strain curve of wool, they gave worsted fabrics having the unique crisp, yet soft feel of wool. Fortunately, they still retain the liveliness and wrinkle-resistance which characterized the filament fabrics. Such fibers give excellent performance in worsted fabrics, such as that used in the tropical worsted suit shown in Figure 19. This suit was worn 18 times and washed in a mechanical washer three times since it was last ironed.

Acetate staple also approximates the stress-strain curve of wool in the critical range of elongations. "Orlon" acrylic fiber departs further from the curve for wool.

## WARMTH OR COOLNESS

One cannot discuss the synthesis of wool-like fibers for long without someone posing the question, "Are they as warm as wool?" When one reviews the physical laws ordinarily believed to control the effectiveness of insulating materials, one is led to believe that the effectiveness of a fabric as a barrier to heat transfer will be mainly a function of the volume of air entrapped within its structure and will be largely independent of the heat-transfer characteristics of the polymer making up the fiber. On this basis one would expect that fibers which produce fabrics as bulky as wool fabrics, and which retain their bulk under service conditions as well as wool fabrics do, will produce fabrics "as warm as wool."

To test these theoretical predictions is much more difficult than would appear on the surface. The effectiveness of a fabric as a barrier to heat transfer is a very critical function of the structure of the fabric, the environmental conditions, and the manner in which the fabric is used as an insulator. For example, in Figure 20 are plotted the rates of heat transfer through two fabrics, a light weight, but rather tightly constucted, nylon shirting fabric and a rather heavy, but porous wool suiting fabric, as a function of the distance between the fabric and the hot surface it is insulating. At zero air gap, the wool fabric shows substantially better insulating properties as one would expect. However, with an air gap of $^1/_2$ inch between the fabric and the surface it is insulating, the nylon fabric offers substantially more resistance to convective heat loss than does the wool fabric. In the face of an air current of about 200 f.p.m. under which these tests were run, the porosity of the wool fabric apparently allows sufficient air to penetrate the fabric to destroy the effectiveness as an insulator of the $^1/_2$-inch air gap behind the fabric. This was not true in the case of the tightly constructed nylon shirting fabric whose insulating properties thereby profited greatly by the still air layer entrapped beneath it.

This problem of the warmth of a garment is just one phase of a more general problem of the comfort of clothing. Clothing comfort has been the subject of a fundamental study by several members of our Textile Research Division since 1950. There have been two angles to the attack, (1) a study of the physics of heat transfer through fabrics, and (2) a physiological study of the comfort of human subjects clad in different garments, exposed to different environments. In the latter study skin temperature, skin wetness, perspiration loss and heart rate served as physiological parameters by which the response of the human body was measured. These studies have been far too complex to warrant reviewing here, but early experimental data bear out the general conclusion that the warmth (or coolness) of a garment is principally a function of the construction of the garment, the construction of the fabric (particularly bulk and porosity) from which it is made and nature of the environment (air temperature, wall temperature, wind velocity, relative humidity, etc.), and is substantially independent of the properties of the fiber making up the fabric except in so far as these control fabric construction through geometric or resil-

[5] HOFFMAN, R. M., *Textile Research J.*, **18**, 141 (1948); BESTE, L. F., AND R. M. HOFFMAN, *ibid.*, **20**, 441 (1950).

**Figure 19. Tropical Worsted Suit of "Dacron" Polyester Fiber (Worn 18 times and washed 3 times since the last pressing)**

ience properties. These studies lead us to believe that if the bulk and resilience properties of a fiber are in an attractive range, it can be used to construct very warm fabrics. Conversely, cool fabrics can be constructed from any fiber.

Thus, by way of summary, the way has been opened for the manufacture of both summer and year-round suits matching or excelling the principal functional properties of wool suits.

## DYEING AND OTHER PROBLEMS

Nylon can be dyed readily with more classes of dyes than are applicable to any other commercial fiber.[6] Consequently, dyeing problems connected with the use of this fiber have been solved largely by selecting dyes to obtain the desired fastness properties. On the other hand, not so many years ago polyacrylonitrile and polyethylene terephthalate fibers, particularly the highly oriented filament yarns, were considered practically undyeable. The dyeing of these fibers was attacked from all possible angles, from the angle of synthesizing new dyes, the development of new dyeing methods, and by modification of the fiber. The first two of these three approaches turned out to be the most attractive. Progress was made at a phenomenal rate. Today both fibers can be dyed to a range of fast shades adequate for initial commercialization. Progress is continuing at a rapid rate.

Acrylic fibers were found[6, 7, 8] to have an affinity for cuprous ions, absorption of which rendered them dyeable with acid colors. Cuprous ions are believed to coordinate with nitrile groups of the polymer, thus providing sites within the fiber to which dye molecules can affix themselves. This technique has been perfected to the point where a full range of colors can be applied to "Orlon" staple having light- and wash-fastness equivalent to good wool dyes on wool.

"Orlon" acrylic fiber has affinity for basic colors. These colors are noted for their brilliance, but on other fibers have very poor light-fastness properties. On "Orlon," however, selected basic colors have relatively good fastness, and this fact opens the way to the union dyeing of blends of "Orlon"/wool, basic colors being applied to the "Orlon" and acid dyes to the wool. Such blends cannot be union-dyed with acid dyes alone, using cuprous irons to impart dye-affinity to the "Orlon" because under such conditions most of the dye goes onto the wool.

Acetate dyes give light shades on "Orlon" with good wash-fastness and moderate light-fastness. "Orlon" has affinity for certain vat dyes, particularly those of the indigoid and thioindigoid classes. It has surprising affinity for indigo in the leuco form from an acid suspension, and a good fast navy blue can be obtained in this manner.

[6] Turnbull, S. G., Jr., *Am. Dyestuff Reporter*, **41**, 75 (1952).
[7] Feild, T. A., Jr., and G. H. Fremon, *Textile Research J.*, **21**, 531 (1951).
[8] Blaker, R. H., and J. F. Laucius, *Am. Dyestuff Reporter*, **41**, 39 (1952).

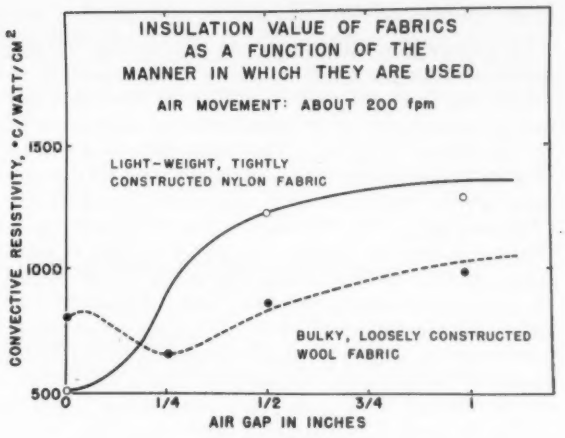


Figure 20

Penetration of dyes into "Orlon" is greatly assisted by conducting the dyeing under pressure at temperatures of the order of 120°C. Staple top, yarn, and knit goods are now being dyed commercially under pressure, and by the time this paper appears in print methods for dyeing fabrics under pressure should have been perfected.

The problem of dyeing "Dacron" boiled down to the problem of selecting and synthesizing dispersed colors with good fastness on the fiber and to finding ways and means to get these dyes into the fiber. Three such ways were found to assist penetration: (1) the use of swelling agents in the dye bath, for example, orthophenylphenol, (2) dyeing above the boiling point of water under pressure, and (3) padding the dye onto the fabric in a uniform manner, followed with a dry heat treatment at an elevated temperature under which condition the dye migrates into the fiber. By such techniques a full range of dispersed colors can be applied to "Dacron" which have light- and wash-fastness in the same range as the fastness of vat dyes on cotton.

The problem of pilling, mentioned earlier in connection with "Orlon," has been also studied in fabrics containing nylon and "Dacron." It has been found that pilling will not occur if the fabric is properly constructed and finished.

Static is another problem which stems from water-insensitivity. On cold, dry days, garments from these new synthetics may cling objectionably. Semipermanent antistatics are just now making their appearance.

Static and a number of other problems are minimized when the fibers are used in blends. When the blend contains 50 per cent or more of the new synthetic a large proportion of the ease-of-care values of the synthetic carries through to the blend fabric. Consequently, this approach to the problem is proving very popular.

Having seen this much progress, it is reasonably certain that one by one the remaining problems will be solved.

## SCIENCE AND INDUSTRY

It is clear from this discussion that during the past quarter-century a good start has been made toward uncovering the principal variables in fiber synthesis and in applying them to meet the more obvious needs of the textile industry. The rudiments of a science of fiber synthesis are clearly apparent, and its development will be continued by the synthetic fiber industry. Many segments of the chemical industry are now joining the search for new fibers. As each new fiber is introduced, the problem of identifying another fiber worthy of commercialization becomes more difficult.[9] This poses new scientific problems and further opportunities for research. Thus industrial research is changing the nature of competition, widening its scope and increasing its tempo. This is the "new competition" spurred by the research laboratories of large companies, which has been so well described by David Lilienthal.[10]

To return to the original theme of this review, we find ourselves in the midst of a textile revolution "sparked" by research scientists. Scientists have discovered the new fibers. Scientists are "tailoring" them to meet the needs of the ultimate consumer. Scientists are placing the fibers in production. Scientists will work out the problems associated with fabric and garment production. Some of these scientists will serve in management positions. The term "research scientists" is used advisedly, because the industry employs a wide spectrum of research scientists, including organic chemists, physical chemists, chemical engineers, mechanical engineers, electrical engineers, and physicists. The type of research facing these men and women varies all the way from highly fundamental problems to highly practical, plant-research studies. Thus the industry offers to a wide variety of scientists the opportunity to have a hand in one of the industrial revolutions of our time and the unfolding of a new branch of science. In so far as their ideas are embodied in fibers and textiles, they are tested not only in the laboratory but also in the market place.

The new synthetic fibers have spectacularly useful properties. Relatively small quantities of these fibers have as yet been produced. Most ultimate consumers are quite unaware of the advances that lie in store for them. In fact, the textile industry is only beginning to be aware of the opportunities facing it. It seems clear that the arts of fabric and garment design which thrive on variety should now flower as they never have before. During the course of a relatively few years designers have witnessed their degrees of freedom roughly doubled by the appearance of new fibers. Consequently the present size of the synthetic fiber industry represents only a beginning. All signs point toward a revolutionary expansion in the production of synthetic fibers and novel products based thereon.

## ACKNOWLEDGMENT

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[9] HECKERT, W. W., "The selection of fiber monomers," *Ind. & Eng. Chem.*, **44**, 2103 (1952).

[10] LILIENTHAL, D. E., "Toward a new policy of bigness," *Collier's*, May 31 to June 28, 1952 (Book to be published by Harper's).

# A MICRO PORPHYRIN TEST FOR BLOOD[1]

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ALTHOUGH it has been a well-known fact since 1871[2] that hemoglobin can be converted to protoporphyrin which is easily detected by its red fluorescence under ultraviolet light, this reaction has only recently been employed in qualitative and quantitative clinical work[3] and has not been included in any laboratory manual of biochemistry. For the latter purpose this report has been written.

When a blood sample is boiled with a solution of hydrazine dihydrochloride in glacial acetic acid, the former reagent converts hemoglobin into porphyrin and the latter keeps proteins in solution, and therefore the red fluorescence is easily observed.

The reagent was prepared by dissolving 1 g. of hydrazine dihydrochloride in a mixture containing 50 ml. of glacial acetic acid and 50 ml. of 0.1 *N* hydrochloric acid. A blood sample of 0.01 ml. was taken by a Thomas type blood-diluting pipet and diluted to 50 ml. in a volumetric flask. This solution had a dilution 1:5,000 and was used as a stock solution for preparing other dilutions as follows: 1:10,000; 1:20,000; 1:30,000; and 1:50,000. Samples of 0.1 ml. of each dilution were placed in test tubes of 75 × 12 mm. and respectively mixed with 6 drops of the reagent. They were heated in a boiling water bath for 3 minutes and then

[1] The work was supported by a research grant from The National Institutes of Health, Public Health Service.

[2] HOPPE-SEYLER, F., *Medizin-chem. Untersuchungen*, Nos. 1–4 (1871).

[3] BRUGSCH, J., *Z. ges. Inn. Med.*, **2**, 191, 454 (1947).

viewed under a mineral light of 3660 Å. side by side with a control containing only the reagent. From several blood samples it was found that 0.1 ml. of the dilution as low as 1:20,000 gave a visible red fluorescence. The sensitivity of the porphyrin test for blood as found above, 1:200,000, is comparable with other tests[4] and should be useful in the detection of blood stains.

[4] Grodsky, M., K. Wright, and P. L. Kirk, *J. Criminal Law, Criminology and Police Sci., Northwestern Univ.*, **42**, 95–104 (1951).

## A CONTINUOUS LIQUID–LIQUID EXTRACTION APPARATUS

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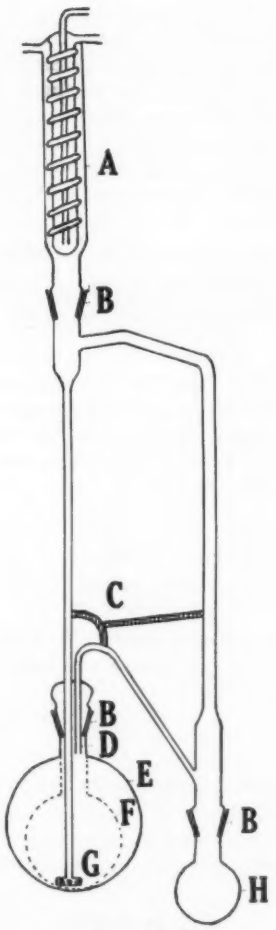
The literature contains diagrams and descriptions of several different designs of equipment which can be used for continuous liquid–liquid extraction. The Friedrichs extractor is very useful for small amounts of material but is not readily adaptable to large or variable quantities.[2] Others which are described use rubber stoppers which may be very undesirable.[3, 4, 5] Some of those described require considerable time for assembly.[3–6] Still another seems to be ideal for working with very large quantities but is more difficult to use with small or varying amounts of material.[7]

Recently this Journal published a diagram of an apparatus designed for continuous extraction but which might prove difficult to fabricate in the average laboratory.[8]

The apparatus shown in the accompanying diagram, as designed and constructed in this laboratory, is not difficult to fabricate; it is easy to assemble, and can be used with flasks of varying size. All connections are ground-glass joints of standard taper, 24/40. Flasks of 1–, 2–, and 3–liter capacity have been used with the apparatus by varying the length of the neck on the flask. The 3–liter flask, E, has a very short neck, whereas the 1–liter flask, F, has a neck which is 11.5 cm. in length. It has not been necessary to use any mechanical stirring; however, stirring might be very conveniently carried out by making the bubbler, G, shorter and then using a magnetic stirrer.

Ether is boiled in flask H and the vapors rise to an efficient condenser, A. The liquid ether is distributed throughout the mixture by the bubbler, G. The ether carrying the compound which has been extracted is then returned to the boiling flask. The apparatus has been used continuously for long periods without appreciable loss of material. Solid glass rods, C, are used to strengthen the apparatus.



Liquid-Liquid Extractor

[1] Associate Professor of Chemistry, Elon College, North Carolina. On leave of absence.

[2] Weiner, Nathan, "Organic Syntheses," John Wiley & Sons, Inc., New York, **1944**, Coll. Vol. II, p. 378.

[3] Aston, J. G., *et. al.*, "Organic Syntheses," John Wiley & Sons, Inc., **1943**, Vol. 23, p. 49.

[4] Campbell, K. N., and A. H. Sommers, "Organic Syntheses," John Wiley & Sons, Inc., New York, **1948**, Vol. 28, p. 66.

[5] Wilson, W. C., "Organic Syntheses," 2nd ed., John Wiley & Sons, Inc., New York, **1941**, Coll. Vol. I, p. 277.

[6] Cox, G. J., and Harriette King, "Organic Syntheses," John Wiley & Sons, Inc., New York, **1944**, Coll. Vol. II, p. 615.

[7] Pearl, I. A., *Ind. and Eng. Chem., Anal. Ed.*, **16**, 62 (1942).

[8] Holliman, F. G., J. Chem. Educ., **29**, 96 (1952).

# SOME THERMODYNAMIC ASPECTS OF REACTION KINETICS

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With the ever-growing volume of information available on reaction rates it has become increasingly important to have an appreciation of the scope and limitations of kinetic studies. To this end an understanding of the thermodynamic basis of reaction rates is an invaluable aid. There have been several independent approaches to this problem, differing in scope and success of their applications. The earliest approach which we will consider here is that of Brönsted and Bjerrum.[2] These authors suggested, separately, an equilibrium between reactants and some form of intermediate. This intermediate was presumed to change irreversibly into the products. Thus, if the reactants are designated as A, B, . . . and the intermediate as M, the reaction was formulated as

$$A + B + \ldots \rightleftarrows M \rightarrow \text{products}$$

The rate of this reaction, $R$, was postulated to be proportional to the concentration, $c_M$, of M. Thus,

$$R = kc_M \tag{1}$$

In the case where there is a deviation from ideality in the system, the thermodynamic equilibrium constant must be formulated in terms of the fugacities or activities, denoted by $a$, of the components. In terms of the activities

$$K = \frac{a_M}{a_A a_B \ldots} \tag{2}$$

$$= \frac{c_M \alpha_M}{a_A a_B \ldots} \tag{3}$$

where $\alpha_M$ is the activity coefficient of M. If we solve for $c_M$ from (3) and substitute the value in (1) we obtain the rate equation

$$R = kK \frac{a_A a_B \ldots}{\alpha_M} \tag{4}$$

Also, if we follow standard procedure in kinetic studies and put

$$R = k' c_A c_B \ldots \tag{5}$$

then

$$k' = kK \frac{\alpha_A \alpha_B \ldots}{\alpha_M} \tag{6}$$

Equations (4) and (6), since rederived in more sophisticated ways, have been widely utilized.

## THEORY OF ABSOLUTE REACTION RATES

*Statement of the Theory.* A more complex and more fruitful formulation has been that of Eyring and his co-workers.[3] Application of this theory requires the construction of a potential energy surface. Such a surface lies in a space in which one coordinate represents the total potential energy of the system, and each other coordinate corresponds to one degree of freedom involved in the reaction. According to the theory a chemical reaction can, usually, be characterized by a path, lying on the surface, which passes in a continuous manner from the initial configuration to the final configuration. The reaction can be taken as proceeding along the most favorable path. There is some intermediate configuration on this path that is critical for the reaction, in that, if the system attains this configuration, the probability of its passing into the final state (products) is high. This critical configuration is termed the "activated complex" or "transition state" and, in general, straddles the point of highest energy on the path. In order that the transition state may include a finite population it is described as occupying a finite, but arbitrary, length $\delta$ along the path.

*Partition Functions.* From statistical mechanics there have come functions known as molecular partition functions. The partition function, $F$, per given volume of a certain molecular species is a measure of the probability of the occurrence of molecules of that species in the given volume. It is often possible to separate the molecular energy into independent vibrational, rotational, translational, electronic, etc., energies. The partition function is then given by

$$F = f_{vib.} f_{rot.} f_{trans.} f_{el.} \ldots$$

where the $f$'s are the partition functions associated with the particular energy types. The translational partition function, for example, is

$$f_{trans.} = \frac{(2\pi mkT)^{3/2} V}{h^3} \tag{7}$$

where $V$ is the volume of the system, $m$ the molecular mass, $k$ is Boltzmann's constant, and $h$ is Planck's constant.

[1] U. S. Public Health Predoctoral Fellow, 1950–52. Present address: Department of Chemistry, The Florida State University, Tallahassee, Florida.

[2] For a full description see Amis, E. S., "Kinetics of Chemical Change in Solution," The Macmillan Co., New York, 1949, Chap. IV

[3] Glasstone, S., K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, 1941. There has been a parallel development in rate theory due to the work of M. G. Evans and M. Polanyi in England.

Since the partition functions are measures of volume concentrations it is possible to express concentration equilibrium constants in terms of these functions. In order to do this it is convenient to use partition functions in which all energies are measured from the zero-point energies. Then, for the equilibrium

$$A + B + \ldots \rightleftarrows M + N + \ldots$$

the concentration equilibrium constant is

$$K_c = \frac{F_M F_N \ldots}{F_A F_B \ldots} e^{-E_0/RT} \tag{8}$$

where $E_0$ is the difference between the sums of the zero-point energies of M, N, . . . and of A, B, . . . .

*Formulation of the Theory.* Consider a reaction in which reactants A, B, . . . proceed through a transition state, M*, to products. The rate of this reaction is given by the product of the concentration of the transition state and the frequency of passage from the transition state to the final configuration. The species which populates the transition state differs from normal molecules in that one vibrational is replaced by one translational degree of freedom. It is convenient to factor out the partition function corresponding to this degree of freedom from the concentration term. Thus,

$$c_*' = c_* \frac{(2\pi m^* kT)^{1/2}\delta}{h} \tag{9}$$

where $c_*'$ is the true concentration of the transition state. It can be shown[4] that the frequency of crossing the potential barrier is

$$\left(\frac{kT}{2\pi m^*}\right)^{1/2} \frac{1}{\delta}$$

Then the rate expression reduces to

$$\begin{aligned} R &= c_* \frac{kT}{h} \\ &= k' c_A c_B \ldots \end{aligned} \tag{10}$$

and

$$k' = \frac{kT}{h} \frac{c_*}{c_A c_B \ldots} \tag{11}$$

If equilibrium is assumed between reactants and transition state, and $K_c{}^{++}$ is the corresponding concentration equilibrium constant,

$$k' = \frac{kT}{h} K_c{}^* \tag{12}$$

$$= \frac{kT}{h} \frac{F^*}{F_A F_B \ldots} e^{-E_0/RT} \tag{13}$$

where $F^*$ is the partition function, excluding one translational degree of freedom, for the transition state.

*Comments on the Theory.* There are certain aspects of this treatment that require closer scrutiny at this stage. It is general practice to include on the right hand sides of equations (10) to (13) a "transmission coefficient," to allow for the possibility of reaction not proceeding to completion even when the configuration of the transition state is attained. However, for many reactions the value of this coefficient is close to unity. For these reactions, then, the transition state always has a momentum greater in the forward than in the reverse direction, a property not held by normal molecules. Thus, although the equilibrium constants may accurately describe the relative concentrations of reactants and transition state, it does not indicate a "normal" energy distribution amongst these species.[5]

In addition, $c_*$ and $F^*$ are highly artificial quantities, and $K_c{}^*$, derived by their use, does not have the dimensions of a true equilibrium constant. On the other hand, by use of an appropriate value for $\delta$, $f_{trans.}$ for translation along the reaction coordinate can be made equal to unity. For this special case $K_c{}^*$ becomes equal in value to the true equilibrium constant.

It is possible to derive rate equation (13) without an initial assumption of equilibrium between reactants and transition state.[6] Nevertheless, there has been considerable discussion as to whether such an equilibrium concentration distribution can be maintained undisturbed while reaction proceeds. It seems, however, that small deviations from this distribution will not cause large variations from the calculated rate.

*Deviations from Ideality in the System.* When sufficient spectroscopic data is available it is feasible to calculate $F_A$, $F_B$, . . . and to obtain an approximate value for $F^*$. In such cases it is possible, by use of equation (13), to calculate the rates of gas phase reactions. When the partition functions are not available, as is the case for reactions in solution, the rates are no longer thus calculable. It is to be stressed that this limitation is imposed by our lack of understanding of the partition functions for dissolved molecules.

In such cases, where allowance must be made for possible deviations from "ideality," the thermodynamic equilibrium constant, $K^*$, must be expressed in terms of activities. It is understood that all activities are referred to the same standard state. Then,

$$K^{++} = \frac{a^*}{a_A a_B \ldots} \tag{14}$$

Solving for $c_*$, as before, and substituting in (10), the rate equation becomes

$$R = \frac{kT}{h} K^* \frac{a_A a_B \ldots}{a^*} \tag{15}$$

which is of the same form as the Brönsted-Bjerrum equation, (4). The transmission coefficient is left out for simplicity. From (15) the specific rate constant is

$$k' = \frac{kT}{h} K^* \frac{\alpha_A \alpha_B \ldots}{\alpha^*} \tag{16}$$

[4] *Ibid.*, p. 186.

[5] For an elaboration of this aspect see: PRIGOGINE, I., AND A. MERTENS in "Contribution to the Study of Molecular Structure," Maison Desoer, Liege, 1947–48, p. 275. Compare with HIRSCHFELDER, J., AND E. WIGNER, *J. Chem. Phys.*, **7**, 616 (1939).

[6] EYRING, H., J. WALTER, AND G. E. KIMBALL, "Quantum Chemistry," John Wiley & Sons, Inc., New York, **1944**, p. 299.

## APPLICATIONS

*Pre-equilibration.* Equation (16) is most readily applied to reactions involving ions, where values for the activity coefficients are calculable by the Debye-Hückel method. The validity of (16) has been checked repeatedly, for such reactions, by experimental determinations of the dependence of rate on ionic strength and dielectric constant. For the reaction

$$A + B \rightarrow \text{products}$$

the equations derived from and used in checking (16) are generally:[7]

$$\ln k' = \ln k'_0 + 2Cz_Az_B\sqrt{\mu} \text{ (ionic strength dependence)} \quad (17)$$

and

$$\frac{d \ln k_0'}{d(1/D)} = \frac{e^2 z_A z_B}{kTr} \text{ (dielectric constant dependence)} \quad (18)$$

where $k'_0$ is the rate constant at ionic strength zero; $C$ is a function of the solvent and temperature; $z_A$, $z_B$ are the charges on A, B, respectively; $\mu$ is the ionic strength; $D$, the dielectric constant of bulk solvent; $e$, the electronic charge; and $r$, the distance between A and B in the transition state.

It can be seen from (17) that if $\ln k'$ is plotted against the square root of the ionic strength, the slope of the resultant line is a measure of the product $z_Az_B$, provided $C$ is known. This has been widely utilized in the study of reaction mechanisms. To appreciate the limitations of this method let us consider a reaction where A is a positively charged base and B is an hydrogen ion;

$$A^+ + H^+ \rightarrow \text{products}$$

Is it possible, on the basis of studies on the ionic strength dependence, to distinguish between the three reaction paths listed below?

$$\begin{aligned} A^+ + H^+ &\underset{\text{fast}}{\rightleftharpoons} (AH)^{++} \\ (AH)^{++} &\xrightarrow[\text{slow}]{} \text{products} \end{aligned} \quad (19)$$

$$\begin{aligned} A^+ + H^+ &\xrightarrow[\text{slow}]{} (AH)^{++} \\ (AH)^{++} &\xrightarrow[\text{fast}]{} \text{products} \end{aligned} \quad (20)$$

$$A^+ + H^+ \longrightarrow \text{products} \quad (21)$$

The initial equilibration in (19) is assumed maintained during reaction.

Application of equation (15) to (20) and (21) gives the rate expression

$$\begin{aligned} R &= \frac{kT}{h} K^* \frac{a_{A^+}a_{H^+}}{\alpha^*} \\ k' &= \frac{kT}{h} K^* \frac{\alpha_{A^+}\alpha_{H^+}}{\alpha^*} \end{aligned} \quad (22)$$

Sequence (19) gives us

$$R = \frac{kT}{h} K^* \frac{a_{(AH)^{++}}}{\alpha^*}$$

But, for the first equilibrium

$$K = \frac{a_{(AH)^{++}}}{a_{A^+}a_{H^+}}$$

Therefore,

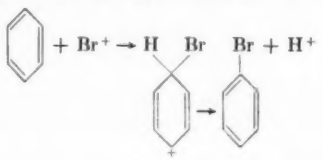
$$\begin{aligned} R &= \frac{kT}{h} K_1^* \frac{a_{A^+}a_{H^+}}{\alpha^*} \\ k' &= \frac{kT}{h} K_1^* \frac{\alpha_{A^+}\alpha_{H^+}}{\alpha^*} \end{aligned} \quad (23)$$

where $K_1^* = K^* K$ is the equilibrium constant for

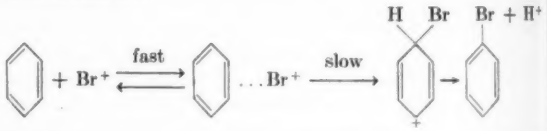
$$A^+ + H^+ \rightleftarrows \text{transition state}$$

Comparing (22) and (23), we see that they have $\alpha_{A^+}\alpha_{H^+}$ in common, and in both $\alpha^*$ refers to a transition state bearing a double positive charge. Thus, the three sequences (19), (20), and (21) would give the same dependence of rate on ionic strength and dielectric constant. It is important to note that if application of equations (17) and (18) to the system gives a value of one for $z_Az_B$, it cannot be concluded that two singly positively charged ions react *in the rate-determining step.*

Similarly, it is generally accepted that bromination of benzene proceeds by a path such as:




It has been suggested that a more complete representation would be:




where the dotted line indicates some form of complexation. Here again, since equilibrium is assumed to be maintained during reaction, it is impossible to distinguish kinetically between these alternatives, unless the complex can be isolated and its properties studied directly.

It can be said, then, that in general there is an unavoidable ambiguity involved in studies of the dependence of rate on activities. This ambiguity is not resolved, but merely ignored, when activity coefficients are assumed equal to unity.

*The Brönsted Relation.* Consider the reaction

$$B + HA_i \underset{\text{slow}}{\rightleftharpoons} BH^+ + A_i^- \xrightarrow[\text{fast}]{} \text{products} + H^+ \quad (24)$$

where B is a base, $HA_i$ an acid catalyst. The rate of such a reaction will be proportional to the concentration of this acid catalyst. The proportionality constant, $k_i$, is known as the catalytic constant of the acid.

It is of interest to compare the catalytic constants of

[7] GLASSTONE, S., K. J. LAIDLER, AND H. EYRING, *op. cit.*, Chap. VIII.

various acids when a fixed substrate is used. Brönsted and Pedersen[8] showed that, provided acids of one charge type are employed, there is a linear relationship between the logarithms of the catalytic and ionization constants. This can be expressed in the form

$$\log k_i = G + x \log K_i \tag{25}$$

where $G$ is a constant and $K_i$ is the equilibrium constant for

$$H_2O + HA_i \rightleftarrows H_3O^+ + A_i^- \tag{26}$$

Thus,

$$K_i = \frac{a_{H_3O^+} a_{A_i^-}}{a_{H_2O} a_{HA_i}} \tag{27}$$

Applying equation (16) we find that the rate of reaction (24) is

$$k' = \frac{kT}{h} K^* \frac{\alpha_{HA}\alpha_B}{\alpha^*} \tag{28}$$

Confining ourselves to a single base and to acids of the same charge type, this equation reduces to

$$k' = FK^*$$

where $F$ is a constant. We might expect a logarithmic relation of the type (25) if there is a fixed relation, in a series of acids, between the free energy of activation and the standard free energy change associated with equilibrium (26). One should, therefore compare (27) with

$$K = \frac{a_{B\cdots H^+} a_{A_i^-}}{a_B a_{HA_i}}$$

where $B \cdots H^+$ represents the transition state for the slow proton transfer. The comparison gives

$$\frac{K}{K_i} = \frac{a_{B\cdots H^+}/a_B}{a_{H_3O^+}/a_{H_2O}}$$

Hammett[9] has shown that in any solution, of reasonably high dielectric constant, the activity coefficient ratio

$$\frac{\alpha_{CH^+}/\alpha_C}{\alpha_{DH^+}/\alpha_D}$$

is a constant, when C and D are two bases of the same charge type. Similarly, the ratio

$$\frac{\alpha_{B\cdots H^+}/\alpha_B}{\alpha_{H_3O^+}/\alpha_{H_2O}}$$

will only be a constant when B is a neutral molecule. Only under these circumstances would we expect $K^{++}$ and $K_i$ to bear a fixed relationship to one another in a series of acids.

Finally, suppose we have a base $C^+$ undergoing the same sequence of reactions as does base B in (24). If, as has been argued above, the catalytic constants of the various acids do not obey the Brönsted relation for this case, is there any property of the acids other than their ionization constants with which correlation is possible? From the discussion in the previous paragraph it would seem that a relation of the form

$$\log k_i = G + x \log K$$

would be valid, where $K$ is the equilibrium constant for

$$D^+ + HA_i \rightleftarrows (DH)^{++} + A_i^-$$

and $D^+$ is any positively charged base. Such equilibrium constants are often measurable spectroscopically.

Application of similar arguments to equation (28) makes it understandable why, when a fixed substrate is used, application of the Brönsted relation gives lines of different slopes for acids of different charge types.

[8] Brönsted, J. N., and K. J. Pedersen, *Z. phys. Chem.*, **108**, 185 (1924).

[9] Hammett, L. P., *Chem. Revs.*, **16**, 67 (1935).

## TRADEMARKS

It seems we laid ourselves open to criticism by failing to pay proper respect to a trademark, in an article in the issue of last December (page 597). When one has to write it many times, it is natural to look for a more convenient name for the sodium salts of ethylenediaminetetraacetic acid and to accept "versene" eagerly for this purpose. But this name is protected by law and must be written Versene with a capital letter. There are many other similar cases, such as Carborundum, Pyrex, Vycor, etc. Attention to such details should be an editor's responsibility, but authors can help.

Sodium acetylsalicylate is aspirin, no matter what manufacturer's name is on the box, but Versene is not the common name for a compound or class of compounds but of a particular product of a particular manufacturer (Bersworth Chemical Company, Framingham, Massachusetts), and not to be confused with Sequestrene, Trilon B, or Complexone II, III, or IV. Trivial names are very important and convenient, but their distinction from trademarks can be very difficult and complicated. But so can all the rest of chemical nomenclature.

# THOMAS PETERS SMITH

## *A Typical Early American Chemist*

**WYNDHAM MILES**
Camden, New Jersey

By the latter half of the eighteenth century the American colonies had reached the point where, to use Benjamin Franklin's phrase, the first drudgery of settlement, which confined the attention of the people to the necessities of life, was pretty well over and there were many with the wealth and leisure to cultivate the arts and add to the common stock of knowledge. The sciences and arts, which had been the possession of a relatively few colonials of fortunate circumstances, began to be taken up by an increasing number of men. Educational institutions were founded, scientific societies were organized, and a growing number of Americans sailed for Europe to study under the masters of the age.

### PHILADELPHIA CHEMICAL SOCIETY

In the field of chemistry there was probably no better spot in North America to study the science than in Philadelphia. At the College a tradition of chemistry was started in the 1750's when lectures, based on Boerhaave's "Elements of Chemistry," Cullen's tables, and Macquer's "Elements of the Theory and Practice of Chemistry," were included in the course of natural philosophy. The tradition was strengthened by the inclusion of chemistry in the curriculum of the Medical Department when it was opened in 1765, and resulted in a Chair of Chemistry, the first professorship of chemistry in North America, being established in the Medical School in 1769. For the people of the town there were series of public lectures given by chemists such as Benjamin Rush, who had studied under Joseph Black at Edinburgh, or itinerant lecturers such as Henry Moyes, the blind Scotch scientist. To enable chemists to keep in touch with one another there were societies such as the American Philosophical Society with its frequent meetings and its *Transactions;* a chemical society organized in 1789 by John Penington (the first chemical society in the United States); and the famous Chemical Society of Philadelphia, founded in 1792, which had among its members Joseph Priestley, James Woodhouse, Adam Seybert, Robert Hare, Nathaniel Chapman, John Redman Coxe, and Charles Caldwell. For reference work or study there were the libraries of the American Philosophical Society, the College, the Library Company of Philadelphia (the oldest circulating library in America), and many private libraries. The town was a center of the book trade, and scientific works were imported from Europe by book sellers, or printed at the presses of Bell, Dobson, Bartram, Oswald, Smith, Adams, Carey, and others. The results of scientific research were printed in the *Transactions of the American Philosophical Society,* in pamphlets issued by the Chemical Society of Philadelphia, in theses of the medical students, and in the literary magazines of the town.

Yet, in spite of its advantages, Philadelphia was only an outpost in the scientific world. Chemicals and equipment were scarce and were usually imported from Europe. For example, when Caspar Wistar became professor of chemistry at the College in 1789 he found there was no equipment available in Philadelphia, and lacking the time to import it from Europe he had to contrive his own. The situation improved in the latter part of the century when common chemicals and simple apparatus could be procured in Philadelphia, but the United States generally remained dependent upon Europe for supplies until well on into the nineteenth century. The greatest disadvantage, however, was the lack of first-rate chemists; men who knew chemistry thoroughly, who could teach it, and who could use it to investigate the controversial problems of the day. American chemistry was really in an elementary state, it tagged along behind Europe like Adams' famous cockboat trailing the British man-of-war. Philadelphia had many men who had attended lectures on chemistry, who could read texts with understanding, and who could perform experiments, but the eighteenth century was almost over before a really good chemist in the person of James Woodhouse, Professor of Chemistry at the University from 1796 to 1809, appeared. Meanwhile, young Philadelphians, along with students from other sections of the country, went abroad to learn advanced chemistry. From the time when John Morgan began teaching chemistry at the Medical School in 1765 until the election of James Woodhouse in 1796, every professor of chemistry studied abroad—Morgan under Cullen; Rush, Wistar, and John Carson under Joseph Black; and James Hutchinson under teachers unknown. Of course many of the men who went abroad studied chemistry only as a minor subject in their education; but there were some whose main purpose it was to learn chemistry and the sciences associated with it, geology and mineralogy. One of these men was Thomas Peters Smith, a young Philadelphian who sailed for Europe in 1800. Smith was not a great figure in American science; as a matter of fact he contributed little

to the advancement of chemistry in this country. Yet, there was so much in his life that was typical of the American scientist of that day—intense patriotism, a desire to help build the United States, study abroad, etc.—that he seems almost like a composite of the American chemists of his time.

## SMITH IN AMERICA

Smith was born in Philadelphia shortly after the start of the Revolution. As is the case with many other early American scientists, we know little of his personal life, and most of our information about his career is derived from his writings and from passing remarks of his contemporaries. Presumably he attended the University, although there is no record that he obtained a degree, for two of the men who were his teachers and who helped to direct his mind toward science were Robert Patterson,[1] Professor of Mathematics, and Benjamin Smith Barton,[2] Professor of Botany. Smith had a vigorous, receptive mind that impressed his friends, one of whom said that by the time he was 18 he was a respectable mathematician, and at 20 he was an eminent chemist.

In the late 1790's Smith joined the Chemical Society of Philadelphia, a lively scientific organization, quite remarkable for that period. There he rubbed elbows with some of the best chemists in the country—James Woodhouse, Adam Seybert, pioneer American mineralogist, Joseph Priestley, John Redman Coxe, who later became Professor of Chemistry at the University, and Robert Hare, who was destined to become one of the greatest American chemists of the nineteenth century. At that time the Society had the custom of holding a special, annual meeting at which one of the members delivered a paper reviewing the progress that had been made in chemistry during the previous year. In 1797 Smith was asked to prepare the review. He accepted the task, but instead of confining himself to the discoveries that had been made in 1796 he enlarged the subject and delivered an address on the progress that had taken place in chemistry since ancient times. The Society was so pleased with Smith's oration that they decided to publish it as a pamphlet under the title, "A Sketch of the Revolutions in Chemistry." This pamphlet is the earliest known publication of an American chemical society, and the first publication on the history of chemistry published in the United States.

Smith's skill in mineralogy and geology led the Society to place him on a committee whose duty it was to analyze minerals and ores sent to it from different sections of the country. The Society made the analyses as a free public service for the purpose of increasing the stock of scientific knowledge relating to the United States, and of drawing the attention of the people to the possibility and desirability of developing the national resources.[3]

In 1798 the Society organized a committee to collect information on niter, an essential ingredient of gunpowder.[4] During this period the United States was anticipating a war with France or England, as well as with the Mediterranean pirates, and there was danger that a shortage of niter would develop as it had two decades before in the Revolution. Smith was placed on the committee, and although the men apparently never published a report, Smith wrote an article, "On niter, and the best means of manufacturing it in the United States," which was published a short time later in one of the Philadelphia magazines.[5]

In 1799 Smith was honored by election to the American Philosophical Society. He attended the meetings regularly, served on its committees, and was finally chosen one of its secretaries. One of his duties in the Society was to judge papers submitted for publication in the *Transactions*, and among these were three written by Joseph Priestley, who was then living in Northumberland.[6]

## IN EUROPE

In 1800 Smith decided to go to Europe to increase his knowledge of mineralogy, geology, and chemistry. On May 27, 1800, he boarded the brig "Roebuck" lying at New Castle and started down the Delaware on the long trip across the Atlantic. Fortunately, Smith kept a journal during most of his travels abroad, and through its pages we can follow his progress back and forth across Europe.[7] He landed at Hamburg near the end of June, and then traveled slowly north

[1] Smith dedicated his first publication, "A Sketch of the Revolutions in Chemistry" (Philadelphia, **1798**), to Patterson, "the instructor of my early youth."

[2] Barton, Professor of Botany and a pupil of Joseph Black, taught chemistry at the University in 1795 while the trustees were trying to persuade Joseph Priestley to accept the professorship. In his "Elements of Botany" (Philadelphia, **1803**, 2nd part, p. 148), he referred to Smith as "My friend and pupil, the late Mr. Thomas P. Smith, whose memory I cherish with a fond respect, and whose death I deplore, as a real loss to science in general, but especially to his country..."

[3] A public notice, advertising the services of the Committee, was published in *Medical Repository*, **1**, 543–4 (1797); *Weekly Magazine of Original Essays, Fugitive Pieces, and Interesting Intelligence*, **1**, 32 (Feb. 3, 1798); *Philadelphia Monthly Magazine*, **1**, 177 (March, 1798); *Constitutional Diary and Philadelphia Evening Adviser*, December, **1799**; *Journal of Natural Philosophy, Chemistry, and the Arts*, **2**, 376 (1799). The notice is reprinted in "Early American Chemical Societies," by W. D. Miles, *Chymia*, **3**, 95–113 (1950).

[4] A note recording the formation and objects of the Committee was published in *Weekly Magazine*, **2**, 3?0 (July 7, 1798); *Medical Repository*, **2**, 111–2 (3rd ed., 1805); *Philadelphia Aurora*, July 13, **1798**. The notice may be found reprinted in "Early American Chemical Societies," by W. D. Miles, *Chymia*, **3**, 95–113 (1950).

[5] *Weekly Magazine*, **2**, 329–31, 374–5 (July 14, 21, **1798**).

[6] *Early Proceedings of the American Philosophical Society... compiled... from the Manuscript Minutes of its Meetings from 1744 to 1838* (Philadelphia, **1884**). *passim*.

[7] The journal which Smith kept in Europe, 1800–02, is in the library of the American Philosophical Society, Philadelphia. It comprises four small volumes, and is written in a hand which is sometimes illegible. The Society has generously granted me use of the journal in drawing up this sketch of Smith. Since the pages of the journal are not numbered, references will be made to dates.

into Denmark and Sweden. He took notes on the geology of the countryside; on the kind, size, and manner of cultivation of the crops; the condition of the domestic animals; the physical appearance, working conditions, and wages of the people; the state of the roads and the construction of bridges. He visited schools, professors, botanic gardens, observatories, museums, art galleries, churches, theaters, monuments, public buildings, and mineral collections. When he discovered mines or factories along his route, he visited them, took notes, and sometimes made sketches. He observed the manufacture of salt at Lüneburg; inspected and described the processes in plants manufacturing chinaware, firearms, and brass; and went underground into copper, silver, and coal mines. While Smith met many famous chemists during his travels, he unfortunately was more intent on taking notes on factories, towns, and the countryside rather than on the scientists; and his impressions of the men, which would be of considerable interest to us, were not recorded in his journal. In Sweden he met Johann Gottlieb Gahn and Peter Jacob Hjelm, friends of Berzelius, Scheele, and Bergman; but of Hjelm he said nothing, and of Gahn only this: "Mr. Gahn is certainly an excellent chymist and mineralogist, and deserves the rank he holds in the scientific world. He joins in their full extent great practical knowledge with philosophical investigation. He is yet in the prime of life, and much is to be expected from him."[8]

From Scandinavia Smith made his way south to France. He remained in Paris for almost half a year, but either he neglected his journal during this period or his notes have been lost. His journal contains the résumé of a course in mineralogy, written in French, which are probably the notes of lectures which he attended in Paris, and also notes, written in English, of four lectures of a course of docimacy given by Louis Nicolas Vauquelin. On April 25, 1801, Smith wrote: "At length after a residence of 5 months and 12 days I have escaped from Paris . . .to escape from the dirty noisy streets of Paris is a luxury only to be known by experience."

Going south he visited a gunpowder factory and made notes of the manufacturing process and the recipe used. Near Moulins he went to the local school where he tried to borrow some ammonium oxalate for use as a reagent: "On asking the professor . . .he said he had none, that he had made some 2 years ago but that it was [a] long time since it was all gone! There was scarcely a compleat instrument for physical or chemical experiments there. The professor himself neither appears to possess very great knowledge or enthusiasm. His course continues 2 years. They had none of the scientific periodical publications."[9]

Continuing south he inspected a niter factory, where he noted the operations were "tolerably well described in Fourcroy."[10] In Clermont he visited the central school where a considerable number of students attended the chemistry course, and there was "a good laboratory, the room very handsome and large, and a number of other rooms well supplied with instruments and agents."[11] At this period France was ahead of other European countries and America in chemical education, and it is unfortunate that Smith did not make comparisons of schools in different countries, and leave more details.

In the neighborhood of Clermont were the extinct volcanos made famous in geology by Jean Guettard and Nicolas Desmarest, and the Puy de Dôme used by Blaise Pascal for experiments with the barometer. Smith spent several days exploring the region. Then he proceeded to Lyons where he found the professor of chemistry not "very profound in his post of science."[12]

Smith could not leave Europe without visiting Switzerland, so he headed for the Alps where he spent some time climbing and studying the mountains. Finally he started down the Rhine to Rotterdam, and embarked for Yarmouth, England, where he landed in October 1801. In England his notes on factories and processes became so detailed that one wonders how he managed to get some of his information from the managers. He constantly searched for devices, machines, and processes which would be useful in America, and in his journal he noted some of the desiderata: "The best plan of boats to navigate in shallow water and be brought up empty. They would be of great use in the Schuylkill to Phila. . . . What is the best method of making coke now in use? In what state should it be for various purposes. The new method of making malleable iron—glass houses, vinegar distilleries, brewery. The best kind of carts for the American roads."

He visited the glass works at Bristol where the men "complain much of cheating in American potash";[13] he examined copper and lead works; tin plate, clay pipe, and porcelain factories; and the Soho engineering works of Matthew Boulton and James Watt at Birmingham. He spent several days with Watt, examining his collection of minerals, inspecting machinery, and visiting a salt works. He went to a coke plant and noted the manufacture of coke from coal, both in open air and closed retorts. Near Birmingham lived the chemist James Keir, who operated a chemical works and a coal mine. Smith was the guest of Keir and inspected his property. Horse railroads were then in use around English coal mines, and Smith, sensing the utility of such a rapid, labor-saving method of transportation in the United States took detailed measurements and made sketches of the road and trucks.

One of Smith's trips, a visit to the iron works of William Reynolds who made "the best iron and steel

[8] SMITH, T. P., *Journal*, Sept. 6, 1800.
[9] SMITH, T. P., *Journal*, May 1801.
[10] SMITH, T. P., *Journal*, May 21, 1801.
[11] SMITH, T. P., *Journal*, May 24, 1801.
[12] SMITH, T. P., *Journal*, June 9, 10, 1801.
[13] SMITH, T. P., *Journal*, November 4, 1801.

in England," resulted in an article which Smith wrote for the *Journal des Mines*:[14] "Note sur la fabrication du fer et de l'acier avec la houille, d'après les procédés de M. Wm. Reynolds, pratiqués, à Coal-brookdale en Angleterre."

In his travels Smith became acquainted with the English chemist Charles Hatchett, the discoverer of the element columbium. Hatchett had found columbium in a specimen of the mineral columbite, which had been sent from Connecticut by Governor John Winthrop the Younger many years before. His research was hampered by the small quantity of the mineral, and he was elated when he met Smith who seemed like the ideal person to obtain more of the scarce substance. In the article announcing the discovery of the new element, Hatchett wrote:[15]

> My researches into the properties of this metal, have of course been much limited by the smallness of the quantity which I had to operate upon; but I flatter myself that more of the ore may soon be procured from the Massachuset mines, particularly as a gentleman now in England, (Mr. Smith, Secretary to the American Philosophical Society) has obligingly offered his assistance on this occasion.

Besides offering to obtain columbite for Hatchett, Smith also made arrangements to exchange American and European minerals with Gahn and Hjelm in Sweden, Van Marum in Holland, Brongniart in France, and others.

## RETURN TRIP

At the end of 1801 Smith left England and returned to France. At this point his journal ends, either being discontinued by Smith or being lost. He remained in Europe until August 1802, and then started back to the United States with a large collection of mineralogical specimens and his head crammed with valuable scientific and technical information. As his ship neared latitude 41°, longitude 46°, in the North Atlantic one of the cannon on board exploded and wounded Smith mortally. With a premonition of death hanging over him, he made a will bequeathing his specimens and journals to the American Philosophical Society:[16]

> To the American Philosophical Society my collection of minerals with the proper catalogues to be found among my papers, to be arranged by them, so as to serve as a scientific collection, but more particularly in a geological & manufacturing point of view. They will find among my papers descriptions of the various chemical manufacturies, such as iron, copper, pottery, etc., as carried on in the various manufactories of Europe I have visited. References are made to such of the specimens as relate to manufactories, which they will find properly noticed. Should they find any information therein contained useful to the manufactories of my country, I beg them to publish them.

Smith lingered for a time, and finally died on September 22, 1802, without seeing again the country he loved. An unknown contemporary, who knew the young man quite well, wrote a brief and touching obituary:[17]

> Died on the 22nd ultimo, at sea, Thomas P. Smith, in consequence of the bursting of a gun.
>
> Few men merit, and still fewer obtain, a long posthumous fame. Their virtues and talents are generally derived from local or temporary events, with the benefits of which they are forgotten. But the subject of these remarks lived not for himself, the particular spot that gave him birth, or the country of which he was proud to be a citizen. His heart exulted in the happiness, and sympathized in the miseries, of all mankind; while his mind exerted its great energies in their service.
>
> Before he reached the period of manhood, he abandoned the frivolous sports of youth, and applied himself to science. With but feeble advantages of education, at eighteen he was a respectable mathematician, and at twenty an eminent chemist. From this period, nature, in all her forms, attracted his attention, and he incessantly mingled the labours of the closet with an observation penetrating, practical and profound. Shaking off the dull logic and inglorious trammels of the schools, his mind disdained other materials of judgment than well-attested facts, analyzed and applied by himself.
>
> Though fascinated to enthusiasm with the charms of natural science, he was not regardless of moral knowledge. He was an early, uniform, inflexible disciple of republican liberty; in his devotion to which he was as firm as the rocks which he so often trod.
>
> Two years ago he went to Europe, principally to extend his qualifications for mineralogical and chemical pursuits. But as the powers of his mind were not circumscribed by common limits, they embraced the whole circle of science. He travelled through England, Germany, France, Sweden, Denmark, and other countries. His associates, wherever he moved, were the learned and the liberal.
>
> With the fruits of wide experience, he sailed, about two months since, for his native land. He had viewed the proudest countries of Europe; but he wrote to his friends that he had seen no country for which he would consent to abandon the United States, where freedom and industry confer happiness. He exulted in the prospect of soon meeting his friends, and in passing in their society, and in literary pursuits, the remainder of his days.
>
> But he has been disappointed. He is gone. With the youth of five and twenty has perished not the blossoms, but the mature fruit of age. Eulogium is often extravagant, but truth sometimes sustains her boldest panegyric; and when she declares that Thomas P. Smith, for science, had no superiors of his age in the United States, and promised, in the progress of life, to have few equals, she pronounces the sacred language of truth.

Death came more often to the young then than it does now, and Smith shared the fate of several other young American chemists—John Penington, George Lee, James Woodhouse—who died before they fulfilled the promise of their youth.

At the time when Smith returned from abroad, there were few men in the United States who had a wider knowledge of European technology than he; and his knowledge, coupled with his industry and enthusiasm, would have made him a valuable acquisition to the scientific stockpile of the country.

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[14] *Journal des Mines*, **13**, 52–6 (1802–3).

[15] HATCHETT, CHARLES, "An analysis of a mineral substance from North America, containing a metal hitherto unknown," *Trans. Roy. Soc.* (*London*), **92**, 49–66 (1802), p. 64.

[16] From a manuscript copy of a portion of Smith's will, dated September 2, 1802, in the library of the American Philosophical Society.

[17] *National Intelligencer, and Washington Advertiser* (Washington, D. C.) October 8, 1802. This obituary was also reprinted in the *Medical Repository*, **6**, 324 (1803).

Because of his early death Smith had little, if any, influence on the development of American chemistry. Yet his patriotism, his wish to do whatever lay within his power to help build the United States into a great nation, his scientific activities in this country, and his study abroad all combine to make him what might be called a typical American chemist of the early days of the republic.

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# SAFETY PRACTICES AND THE CHEMISTRY STOCKROOM[1]

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MUCH has been written concerning the topic "safety" and its various ramifications. It is generally accepted that industrial plant and laboratory safety programs are more extensive than those in evidence at academic institutions. Regardless of the fact that "we know better," our academic research workers and students continue to be involved in accidents which *could* and *should* have been avoided by the establishment and enforcement of proper safety practices and procedures.

In the event of an accident in an academic laboratory the instructor in charge invariably comes to the stockroom for "a chair," "a telephone," "an extra piece of tape," or other item either closely or remotely associated with the accident. In other words, the stock room attendant is generally considered as the "main line of defense" when accidents occur in the laboratory.

During the course of visiting staff members and stockroom personnel at several of our colleges and universities, information concerning interesting safety policies and practices has been obtained. It is believed that a material increase in efficiency and operation of safety programs would result if certain of these were incorporated in the safety programs of other academic institutions.

The stockroom superintendent at many schools is often charged with the maintenance of emergency cabinets as well as issuing and filing "accident report" forms.

In an effort to insure the use of a pay telephone booth, located in the hallway of a building, one school makes a common practice of including a five-cent piece as an essential piece of emergency cabinet "equipment." Such a practice has proved very timely in the event of after-hour accidents when offices containing outside phones were not open. All too often one may have paper money, a quarter or a fifty-cent piece in his pocket, but would be unable to call a doctor, hospital, taxi, or fire department in the event of an emergency.

Certain of our schools require that more than one student be present in any laboratory if working after regular hours. In this manner it is believed one individual would be available to assist another in the event of an accident.

Certain equipment normally stocked in emergency cabinets is sometimes of value to students and staff members in their research programs. Scissors, forceps, and adhesive tape fall into this class of materials. At times certain personnel tend to use such items and "fail" to return them on completing their use. In an effort to eliminate such serious loss of important first-aid equipment, one school has virtually eliminated the

[1] Presented at the 122nd Meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1952.

number of keys for emergency cabinets which are issued to staff members. The bolt on the lock of each cabinet closes behind a microscope slide which is recessed in the framework of the cabinet. In the event of an emergency requiring the use of the materials in a cabinet, one merely breaks the microscope slide using a small hammer attached to each cabinet with a light chain. After breaking the glass slide, the door of the cabinet opens readily. Within each cabinet is a pad of forms one of which must be filled out covering the time and date of opening the case, as well as the names of individuals concerned in and treating the accident case. Thus undue breakage of microscope slides is reduced to a minimum. The broken slide is promptly replaced and the materials used from the cabinet are replenished.

Several schools maintain "accident report forms" in their chemistry department stockrooms. One must be completed for each accident which takes place in the department laboratory. Many of these forms are detailed in nature and include information relative to date, and time of accident, as well as details of its nature. Names of individuals giving first aid as well as those in charge of the laboratory are also requested. A description of the treatment is also desired. Such reports are generally filed with the stockroom attendant or the director of the laboratory as promptly as possible.

Several of our schools have pharmacy-school graduates supervising their stockrooms, while others use pharmacy graduates for the preparation of reagent solutions and the filling of laboratory reagent bottles. Although the task of bottle filling is considered as routine, severe damage to experiments, research programs, and even to personnel can result if the wrong solution is placed in a bottle on a reagent shelf.

The maintenance of a complete stock of first-aid equipment in chemistry department emergency cabinets is a duty often assigned to storeroom personnel. One of our larger schools maintains a loose-leaf notebook record on each such cabinet which is "serviced." One page of this record is assigned to each cabinet. Spaces are provided to indicate date and time of inspection, together with the record of missing items as well as those which are added. All such cabinets are checked at least once a week, with certain units (in popular laboratories) checked at more frequent intervals. The master record book of such inspections is maintained in the office of the superintendent of chemical stocks.

Another school which does not maintain a record of inspection of emergency cabinets has one of its storeroom attendants check every unit daily. (It requires approximately three hours' time to cover 35 cabinets.)

New graduate assistants in chemistry departments at many schools usually have an "orientation meeting" during their early days on a campus. One important phase of such an orientation is a description of the safety and first-aid practices in operation. The storeroom superintendent, or one of his assistants, is generally called upon to outline this topic as well as others with which he is directly concerned.

A few of our schools require the use of safety glasses by all personnel using any of their laboratories. These glasses may be purchased outright through the department stockrooms, or may be obtained on a temporary (annual) loan by signing the proper memoranda at departmental stockrooms. At the end of each school year the stockroom personnel have the responsibility of checking-in these temporarily loaned glasses, as well as reconditioning them for issue the following year. This task includes a disinfecting procedure as well as proper storage; it entails considerable additional work at an extremely busy stockroom period.

Another observation worth mentioning is that the larger stockroom is not always more safety-minded than the smaller unit. I have seen a very small storeroom containing only four drums of volatile solvents in the "solvent portion." Each drum containing a faucet for withdrawing its contents was carefully grounded by attaching a lead wire and battery clip to a near-by water pipe. Such a simple, inexpensive measure virtually eliminates the danger of ignition of flammable solvents from static electrical charges.

Safety literature, technical as well as commercial, invariably finds it way to the desk of the stockroom superintendent. He often serves as a "filter center" for new ideas and items which are made available. Thus he is often responsible for initiating the use or suggesting the adoption of such materials as "safety supports" for cylinders of compressed gases, or new-style portable fire extinguishers, as well as newly developed practices for first-aid treatment, throughout the entire department. Thus the adoption of new safety equipment or first-aid practices frequently depends upon the interest and initiative of the stockroom superintendent.

In spite of his many duties and responsibilities, the chemistry department stockroom superintendent is frequently one of the key individuals associated with safety practices and first-aid procedures in use in our academic institutions. He is doing a commendable job and exhibiting initiative and originality in many institutions. Observations indicate that the extent and degree of "safety mindedness" evident in many schools vary throughout a considerable range. It is believed that many schools could profit by learning of safety practices being used at others. Safety is a topic which we can continually improve upon, and no matter how successful we are or how perfect our current record, we can always make it even better.

# ADIABATIC CHANGES

## *Reversible and Irreversible Changes Involving only Pressure-Volume Work*

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THE formulas for adiabatic changes seem to be stumbling blocks for students in elementary physical chemistry at the junior level, and for seniors and even first-year graduate students in elementary thermodynamics. This is all the more true because examination of several texts in physical chemistry and thermodynamics shows that these formulas are often left as, presumably, moderately difficult exercises for the beginner. It has been my experience that the beginner, struggling to keep his head above water as far as the first law of thermodynamics is concerned, will sink at this point in nine out of ten cases.

In this paper I should like to stress two simple devices which have proved of great value pedagogically in studying adiabatic changes.

The first is to insist that derivations involving adiabatic changes begin with the first law of thermodynamics, preferably in the differential form,

$$dE = Dq - Dw \tag{1}$$

where the exact differential, $dE$, is the difference of the two inexact differentials, $Dq$ and $Dw$.

Unless this is done, the student with a good memory will probably begin with the formula,

$$C_v\,dT = -P\,dV \tag{2}$$

The student with not so good a memory leafs through the book until he finds (2), not stopping to check the conditions under which the formula is valid.

Perhaps the student is not entirely to blame for this, since most textbooks print such formulas so that they stand out plainly from the page, while the qualifying statements which restrict their use, which are as important as the equations themselves, are lost in the accompanying text. It would be a great help to beginners if important restrictions were placed close enough to any formula to form almost an integral part of it.

Beginning then with equation (1) we have, since, for an *adiabatic change*

$$Dq = 0 \tag{3}$$
$$dE = -Dw \tag{4}$$

In general,

$$Dw = P_{surr}\,dV - \mathfrak{F}\,dL - \mathcal{E}\,dZ - \mathfrak{M}\,dI - \gamma\,dA - mgdh - \Sigma Y_i\,d\chi_i \tag{5}$$

where the terms on the right represent, respectively, the work required to change the volume of a system; the work required to stretch a system elastically; to change the electrical charge on a system; to vary the intensity of magnetization; to alter the surface area; to increase or decrease the gravitational potential; and to perform other kinds of work not included in the above.

Usually only, one, or at most two, of these work terms will be important in a given problem, but the student who has been compelled to consider these various work terms and to realize that they can be eliminated only when at least one of the factors in them is zero, will be less likely to imagine that $Dw$ is identical with $P_{surr}dV$, and less flabbergasted when asked to handle a problem where the only work is, say, electrical.

For *adiabatic changes* with *both P-V and electrical work* we have,

$$dE = -P_{surr}\,dV + \mathcal{E}\,dZ \tag{6}$$

and for *adiabatic changes* with *only P-V work*,

$$dE = -P_{surr}dV \tag{7}$$

Use of the symbol $P_{surr}$ for the pressure of the surroundings, the external pressure against which the system operates, is the second simple device which helps the beginner overcome the confusion which inevitably arises over the pressure of the system, $P_{syst}$, occurring in the equation of state of the system, and the pressure of the surroundings, $P_{surr}$, occurring in the differential $PdV$. Without this simple difference in symbols I have found it well nigh impossible to prevent a semiautomatic substitution of $P_{syst}$ for $P_{surr}$. In problems involving irreversible changes, this error is fatal.

A number of problems involving (7) can readily be devised. Although some of these are not of great practical value in themselves, they are of the greatest utility in helping the beginning student develop the ability to think *physically* about his calculus formulas, and to overcome the compartmentalization which has usually arisen, since the student has all too often been required to juggle mathematical symbols with no physical referent. For example, if a block of aluminum undergoes an adiabatic change in which the internal energy has decreased five calories, while the external pressure is constant at two atmospheres, does the

volume increase, decrease, or remain constant? Since $dE$ is negative here, $dV$ must be positive. If desired, the actual volume change may be calculated from the data given, care being taken regarding dimensions.

A troublesome problem for beginners is the calculation of the temperature change for an ideal gas in an *adiabatic, irreversible* process involving *only P-V work.*

Aside from exceptional cases, such as phase changes, it is usually convenient to take the internal energy, $E$, as a function of the temperature and volume so that we have,

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV \tag{8}$$

Substituting in (7) we obtain a general expression from which we can calculate the temperature change in an adiabatic change, involving only $P$-$V$ work:

$$dT = -\frac{\left[\left(\frac{\partial E}{\partial V}\right)_T + P_{surr}\right]}{\left(\frac{\partial E}{\partial T}\right)_V} dV \tag{9}$$

For *only P-V work,*

$$\left(\frac{\partial E}{\partial T}\right)_V = nC_v \tag{10}$$

where $n$ is the number of moles and $C_v$ is the molar heat capacity.

For cases where other than $P$-$V$ work is involved we would have

$$\left(\frac{\partial E}{\partial T}\right)_V = nC_v + \left(\frac{Dw}{dT}\right)_V \tag{11}$$

Ideal gases have $(\partial E/\partial V)_T = 0$, so that (9) becomes, for an adiabatic change of an *ideal gas* with *only P-V work:*

$$dT = -\frac{1}{nC_v} P_{surr}\, dV \tag{12}$$

This equation is useful in pointing out that the temperature drop depends upon the amount of work done by the gas during this change. In a *free expansion,* where $P_{surr}$ is zero by definition, there will be no temperature change.

In *irreversible* processes other than free expansion, where $P_{surr}$ is either constant or variable, equation (12) is the starting point for the calculation of the temperature change.

The general integrated formula will be

$$T_2 - T_1 = -\frac{1}{n}\int_{V_1}^{V_2} \frac{P_{surr}}{C_v}\, dV \tag{13}$$

In the special case of the *adiabatic change* of an *ideal gas,* with *heat capacity independent* of both *temperature* and *volume, with only P-V work* against a *constant external pressure* we obtain,

$$T_2 - T_1 = -\frac{P_{surr}}{nC_v}(V_2 - V_1) \tag{14}$$

In *reversible* expansions the external pressure must always be infinitesimally less than the pressure of the system. Neglecting this infinitesimal difference, we may make the very important substitution for *reversible expansions:*

$$P_{surr} = P_{syst} \tag{15}$$

For an *adiabatic reversible* change of an *ideal gas* with *only P-V work* (9) becomes

$$dT = -\frac{1}{nC_v} P_{syst}\, dV \tag{16}$$

or

$$dT = -\frac{1}{nC_v} nRT\frac{dV}{V} \tag{17}$$

Carrying along the $n$ with the $C_v$ and with the equation of state helps the beginner, who needs this repeated emphasis, to avoid ending at this point with an equation which would imply that the temperature change depends on the number of mols of gas present. This is particularly likely to happen if the double substitution $P = P_{syst} = nRT/V$ is made in (2).

Physically the beginner could easily check to see that the temperature change should be independent of the number of mols present by considering two different containers, one with twice as many mols of gas as the other. By putting the confined gases through the same *relative* volume change, it is easy to see physically that the temperature change should be the same in both cases.

Integration of (17) gives, for the *adiabatic, reversible change* of an *ideal gas* involving *only P-V work* ($C_v$ constant),

$$C_v \ln\frac{T_2}{T_1} = R \ln\frac{V_1}{V_2} \tag{18}$$

The difference between (18) and (13) and (14) emphasizes the necessity of care in distinguishing irreversible, (13) and (14), and reversible, (18), behavior.

The importance of regarding equation (9), rather than (2) or (12) or (16), as the immediate point of departure for adiabatic changes involving only $P$-$V$ work can be seen again if it is a question of calculating, say, the temperature effect for a van der Waals' gas.

One who starts with (16), thinking that it is necessary only to use

$$P_{syst} = \frac{nRT}{V - nb} - \frac{an^2}{V^2} \tag{19}$$

has already thrown away the $(\partial E/\partial V)_T$ term of (9).

To apply (9) we first get $(\partial E/\partial V)_T$ in somewhat more usable form from a "thermodynamic equation of state,"

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P_{syst}}{\partial T}\right)_V - P_{syst} \tag{20}$$

From (19), the equation of state for a van der Waals' gas, we have

$$\left(\frac{\partial P_{syst}}{\partial T}\right)_V = \frac{nR}{V - nb}, \tag{21}$$

so that (20) becomes

$$\left(\frac{\partial E}{\partial V}\right)_T = \frac{nRT}{V - nb} - \frac{nRT}{V - nb} + \frac{an^2}{V^2} = \frac{an^2}{V^2} \tag{22}$$

Substituting (22) into (9) we get for the *irreversible adiabatic expansion* of a *van der Waals' gas* with *only P-V work:*

$$dT = -\frac{\left[\frac{an^2}{V^2} + P_{surr}\right]}{nC_v}\,dV \qquad (23)$$

Comparing (23) with (12) we see that while, for an ideal gas, the temperature change depends only on the external work done (if $C_v$ is constant), there will be a temperature change for a van der Waals' gas even with free expansion.

In a *reversible* expansion we again have $P_{surr}$ equal to $P_{syst}$, and substituting from (19), (23) becomes for the *reversible, adiabatic* expansion of a *van der Waals' gas,* with *only P-V work,*

$$dT = -\frac{nRT}{nC_v(V - nb)} = \frac{RT}{C_v(V - nb)} \qquad (24)$$

Up to this point we have always considered $C_v$ a constant. To help drive home to the beginner that we have been dealing with a special case, it is useful now to consider $C_v$ as at least a linear function of $T$.

Substituting

$$C_v = \alpha + \beta T \qquad (25)$$

into (24) and integrating we have finally, *with the restrictions applying to (19),*

$$\alpha \ln \frac{T_2}{T_1} + \beta(T_2 - T_1) = R \ln \frac{V_1 - nb}{V_2 - nb} \qquad (26)$$

For real gases other than "van der Waals' gases" adiabatic temperature changes may be determined from (9) if $(\partial E/\partial V)_T$ can be obtained from $P$-$V$-$T$ data using equation (20).

A final stumbling block occurs in connection with the integrated form,

$$C_v \ln \frac{T_2}{T_1} = R \ln \frac{V_1}{V_2} \qquad (18)$$

If the temperature change in terms of the pressure rather than the volume is desired, it seems natural for the beginner to substitute from $P_1V_1 = P_2V_2$. Unfortunately, this short cut, while "eliminating" $\frac{V_1}{V_2}$, does not give the correct result,

$$C_p \ln \frac{T_2}{T_1} = R \ln \frac{P_2}{P_1} \qquad (27)$$

The reason that it does not is that one cannot use Boyle's law, which holds at *constant* temperature, to substitute into the righthand side of an equation of which the lefthand side involves a *change* in temperature. The correct substitution is

$$V_i = \frac{nRT_i}{P_i}$$

When this is made, (27) results, using $C_p = C_v + R$.

In this paper I have mentioned the advisability of starting from the first law, using the general work term in beginning the derivation of formulas for adiabatic changes. The value of using different symbols for pressure, according to whether it is the pressure of the system or external pressure of the surroundings, has been stressed.

## ESSAY PRIZES

THE British quarterly scientific review *Endeavour* is offering five prizes (the first is 50 guineas) for an essay, not exceeding 4000 words, on one of the following subjects: (1) Radio-astronomy, (2) Color and chemistry, (3) Biology in world affairs, (4) Science and safety in transport, (5) Science and art, (6) Scientific contributions to medicine, (7) Scientific societies and their role, (8) Power and civilization. The competition is restricted to those whose 25th birthday falls on or after June 1, 1953.

Entries should be addressed to: The Assistant Secretary, British Association for the Advancement of Science, Burlington House, Piccadilly, London, W.1, and the envelope should be marked "*Endeavour* Prize Essay." The latest date for receipt of entries is June 1, 1953. The essays must be typewritten in English and should be submitted without signature, the competitor's name, address, and date of birth being disclosed in a sealed covering letter attached to the essay.

In judging the results special attention will be paid to the originality of the approach to the subject, and to literary style. The essay winning the first prize will be published in *Advancement of Science,* journal of the British Association.

The competition is open to young scientists in the United States and elsewhere.

# SOME CHEMICAL RELICS

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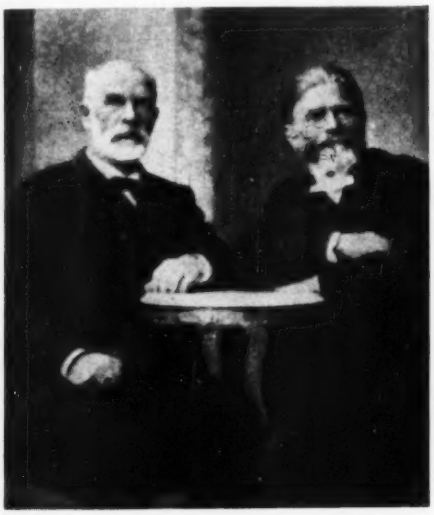
THE names of Peter Waage (1833–1900) and his brother-in-law Cato Maximilian Guldberg (1836–1902) are indissolubly linked in their "Law of Mass Action." Waage was professor of chemistry and director of the chemical laboratory in the University of Christiania (now Oslo). He published a number of smaller papers



C. M. Guldberg and Peter Waage

in various fields of inorganic, organic, and mineral chemistry, and had a good reputation in chemical circles both at home and abroad, especially in England. Guldberg was a mathematician as well as a competent physical chemist. He taught at the Royal Artillery and Engineering School of Norway from 1860 until 1867, when he accepted a lectureship at the university, which, being the only university in Norway at the time, was called the Royal Frederick University. In 1869 he was given the chair of applied mathematics.

The joint researches on chemical affinity were carried out in the university laboratory. The results and the discussions were published in three papers. The first two received little attention because they appeared in the relatively inaccessible *Forhandlinger i Videnskabs-Selskabet i Christiania* (1864, in Norwegian) and as a university publication (in 1867, in French). Consequently, parts of the theory were discovered independently by others. Guldberg and Waage's work really became known to the general chemical public in 1879 when the complete account appeared in the *Journal für praktische Chemie* (in German). The text also appeared in the *Forhandlinger* of 1879 (in Norwegian).[1]

Balance, Silver Bottles, and Ladle Used by Guldberg and Waage

One of the reactions that was studied in detail was the equilibrium:

$$\underset{\text{(solid)}}{BaSO_4} + \underset{\text{(solution)}}{K_2CO_3} \rightleftharpoons \underset{\text{(solid)}}{BaCO_3} + \underset{\text{(solution)}}{K_2SO_4}$$

Since glass is seriously attacked by all except very dilute solutions of potassium carbonate, and especially at high temperatures, they used silver and platinum

Old Chemical Laboratory at the University of Christiania (now Oslo)

bottles in which to carry out the reactions. When working at the boiling point of water, the bottle was closed with a rubber stopper carrying a glass tube about

[1] All three papers are available (in German) in No. 104 of Ostwald's *Klassiker der exacten Wissenschaft*, Leipzig, 1899. An excellent commentary is included there.

0.7 meter long and drawn down to a fine tip at both ends. In this way practically no water was lost during the reaction; the steam condensed in the tube and flowed back. The loss over nine hours heating at 99–100° was only 0.052 g.

The balance used in these "Studies of Chemical Affinity" is preserved in the laboratory at the University of Oslo. Some of the silver bottles and a silver ladle also employed in these researches are also there. The pure silver equipment is badly tarnished, which is only natural in a laboratory atmosphere.

These relics again show that simple equipment combined with devoted and alert minds can yield results of permanent and far-reaching value.

# COUNSELING BY STATISTICS

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SIGNIFICANT progress has been made in preparing tests that assist a guidance counselor in discussing with prospective college freshmen the choice of curriculum that the students must make. In the field of engineering the Pre-Engineering Inventory is outstanding.[1]

Yet the problem of selecting and training prospective engineers is not simply solved. Tests of aptitude cannot predict application. Parental hopes may override test results. The aptitude tests do not as yet give guidance in selecting a particular type of engineering, and the student's somewhat undefined interests may become a major factor in his success or failure. Furthermore, the use for guidance of most test results requires the interpretation of a person trained for such work.

At Lehigh University all engineering freshmen take the same courses although the choice of a branch of engineering is stated at the time of entrance; the change from one curriculum to another up to the beginning of the sophomore year may be done without difficulty. The change from one branch to another after that time involves taking additional courses. Thus, a critical time for helping students to decide either on a change of course or an increased effort within the same course comes during the summer after the freshman year. Rather few of the students, however, are available for personal conferences during that summer.

In Table 1 the time and reason for leaving the curricula of chemistry and chemical engineering are shown for students who did barely passing (D) or failing (F) work in one or both first-year chemistry courses. The period covered is from 1942 to 1949.

The large number of these people who made some sort of change after one semester of the sophomore year is particularly disturbing. It would seem most worth while to be able to give guidance that would push the decision to change, if it must come, forward a semester in the cases where some clue to the desirability of a change can be detected. An earlier decision would save the student time and frustration, and a proper transfer might prevent the necessity of his being dropped for poor scholarship.

The simplest possible guide for men in chemistry and chemical engineering and the most readily available one is the performance in general chemistry. Such a criterion involves some combination of aptitude, application, attitude, and achievement. To determine whether there was any relation between performance in general chemistry and success in the curricula of chemistry and chemical engineering, the records of men

[1] VAUGHN, K. W., *J. Eng. Ed.*, **38**, 114 (1947); **37**, 676 (1946); **36**, 111 (1945); **35**, 161 (1944).

**TABLE 1**

**Semester After Which Students With Poor Records Left The Curricula of Chemistry and Chemical Engineering, Lehigh University, 1942–49.**

| *Semester:* | *2* | *3* | *4* | *5* | *6* | *7* | *8* | *10* | *T* |
|---|---|---|---|---|---|---|---|---|---|
| Dropped for poor scholarship | 3 | 9 | 5 | 2 | 4 | .. | .. | .. | 23 |
| Withdrew from the University | 1 | 1 | 2 | .. | 2 | 1 | 1 | 1 | 9 |
| Transferred to other curricula | 5 | 18 | 7 | 6 | 1 | 1 | .. | .. | 38 |
| Total | 9 | 28 | 14 | 8 | 7 | 2 | 1 | 1 | 70 |
| Per cent | 13 | 40 | 20 | 11 | 10 | 3 | 1 | 1 | 100 |

as far back as the fall semester of 1941—42 through the spring semester of 1948 were studied. Table 2 shows these data and indicates that only one man in ten who did poorly in general chemistry received an engineering degree in chemistry or chemical engineering in the normal period of eight semesters.

Table 3 presents similar data for men who received (D) or (F) in one or more of the four sophomore courses—two laboratory and two lecture—in analytical chemistry. The data cover about the same period as the previous table. A larger per cent of these men received degrees in the usual eight semesters, though such students came principally from those who had only one (D) or (F) in the four courses.

Use of these data as a guidance aid has been made during the summers of 1949, 1950, and 1951. The freshmen and some of the sophomores who had received D's or F's in chemistry courses in the preceding year received a copy of the appropriate table and a letter from the Director of the Curricula pointing out the odds that the men were facing and urging reconsideration of their vocational decision. The Director then urged the men, if they believed that they had originally selected the proper course, to plan a change in study habits or amount of effort in order to avoid the fate of too many of their predecessors. The men were urged to talk to the Director or other faculty members if they so desired.

Such an aid to guidance, either to effect a change of curriculum or to encourage better performance in the present course, has the advantage of presenting the situation in familiar terms. The man himself knows how he did in the courses used as criteria. He knows how conscientiously he went about his work. He can easily visualize men a few years ahead of him and knows that they took about the same courses. He sees how they fared and so can weigh his own prospects. Furthermore, the tables and their meaning can be interpreted, at least fairly accurately, by the layman to whom a battery of tests sounds very impressive but somewhat mysterious. Finally, the guidance or the push toward further guidance can be given at a time when the student is not on the campus.

This guidance device is no more infallible than any other. Of the men graduated from the Department of chemistry and chemical engineering at the three commencements in the school year, 1949—50, twenty-three had had scholastic troubles—one or two extra semesters, needed for graduation or one or more semesters on scholastic probation.

Three of the twenty-three gave no indication in freshman or sophomore chemistry courses that such trouble lay ahead. There was warning in the other twenty cases.

After use during three summers, the device appears to have been reasonably effective. A total of 27 freshmen have received the data and the accompanying letter. Of these 27, to date 19 have changed to another curriculum or have withdrawn from the University. Twelve of these withdrawals or 63 per cent occurred between the freshmen and sophomore years while the rest have taken place later in the men's college careers. This contrasts very favorably with the over-all 13 per cent withdrawal at that time in the preceding eight years. In one of the summers, the letters were not sent out until about the middle of August. Most of the group who stayed in the curricula beyond this summer and subsequently withdrew were in this group. It seems likely that writing earlier in the vacation period might have made the results even more favorable.

A total of 38 sophomores have received the data on sophomores and the corresponding letter. Since they had two years in the curricula already completed, these men were found much less willing to make a change. Of the 38, four left the Department after the sophomore year. Eight additional departures occurred after one or more additional semesters. Eight of the men who stayed made significant improvement in their scholastic performances after they received the letter. Probably the most important positive result of the use of this guidance device with sophomores was a number of serious conferences about scholastic problems that in all probability would not otherwise have taken place.

Our experience indicates that aids to guidance based on the experience of previous students are easier to prepare and use than we had previously realized and that such aids appear to be effective enough to move a good percentage of the students to appropriate action.

**TABLE 2**

**Fate of Men Who Did Barely Passing (D) Or Failing (F) Work In One Or Both First Year Chemistry Courses**

| | | |
|---|---|---|
| Men who continued satisfactorily | | 6 |
| Received degree with no interruption | 1 | |
| Received degree with Armed Service interruption | 5 | |
| Men who continued with trouble | | 50 |
| Transferred: | | |
| to other engineering curricula | 6 | |
| to College of Arts and Science | 4 | |
| to Business College | 10 | |
| Withdrew | 5 | |
| Dropped | 12 | |
| Received degree in nine or more semesters | 13 | |
| Total | | 56 |

**TABLE 3**

**Fate Of Men Who Did Barely Passing (D) Or Failing (F) Work In One Or More of The Four Sophomore Chemistry Courses**

| *No. of Courses:* | *1* | *2* | *3* | *4* | *Total* |
|---|---|---|---|---|---|
| Men who continued satisfactorily | | | | | 33 |
| Received degree—no interruption | 13 | 4 | 0 | 0 | 17 |
| Received degree—Armed Forces interruption | 8 | 6 | 2 | 0 | 16 |
| Men who continued with trouble | | | | | 100 |
| Total transferred: | | | | | 31 |
| to other engineering | 3 | 0 | 0 | 0 | 3 |
| to Arts and Science | 7 | 6 | 3 | 0 | 16 |
| to Business | 3 | 5 | 2 | 1 | 11 |
| to other | 0 | 0 | 1 | 0 | 1 |
| Withdrew | 1 | 4 | 2 | 0 | 7 |
| Dropped | 4 | 8 | 6 | 2 | 20 |
| Received degree after difficulty | 15 | 13 | 11 | 3 | 42 |

# THE STABILITY OF A COMPLEX ION

## *A Laboratory Experiment in Radiochemistry and Ion Exchange*

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THE experiment described in this paper is designed for a laboratory course in advanced physical chemistry. It introduces the student to three important aspects of physical chemistry: (1) the determination of the composition and stability of a complex ion in solution; (2) the use of synthetic organic ion exchangers; and (3) simple radiochemical technique.

The experiment consists in the measurement of the distribution of carrier-free[1] radioactive stontium between a buffered solution containing varying concentrations of citric acid and a cation exchange resin immersed in the solution. The stability quotient of the complex ion formed between $Sr^{++}$ and the citrate ion, $Cit^{3-}$, is calculated from differences in the uptake of $Sr^{++}$ by the cation exchanger from solutions of various citrate concentrations. The measurements are made under simulated physiological conditions, *i. e.*, a pH of 7.25 and ionic strength of 0.16. Practically all of the citric acid is present as a trivalent ion when the pH is greater than 7.0. The theoretical and experimental aspects of ion exchange technique as applied to complex ion studies have already been discussed (*1*, *2*).

### THEORY

The reaction between a cation exchange resin in the sodium form and strontium ion in a solution buffered with a sodium salt can be written:

$$Sr^{++} + 2NaR \rightarrow SrR_2 + 2Na^+ \qquad (1)$$

in which R represents the insoluble anionic part of the cation exchange resin with an assumed charge of $-1$. The concentration of $Sr^{++}$ is negligible in comparison with that of $Na^+$, hence no appreciable change in $Na^+$ concentration in either the solution or resin phases occurs at any time. The equilibrium quotient, $K_q$, for reaction (1) is given by the following mass action expression:

$$K_q = \frac{[SrR_2][Na^+]^2}{[Sr^{++}][NaR]^2} \qquad (2)$$

in which the bracketed terms represent molar concentrations.

The addition of $Cit^{3-}$ to the solution reduces the concentration of $Sr^{++}$ and reduces the uptake of $Sr^{++}$ by the cation exchanger according to the following equation:

$$Sr^{++} + n\ cit^{3-} \rightarrow Sr(Cit)_n^{2-3n} \qquad (3)$$

The formation quotient, $K_f$, for reaction (3) is:

$$K_f = \frac{[Sr(Cit)_n^{2-3n}]}{[Sr^{++}][Cit^{3-}]^n} \qquad (4)$$

The distribution coefficient, $K_d$, is defined as the ratio of concentration of strontium in the resin phase to that in the external solution, thus:

$$K_d = \frac{\%\ \text{Sr in exchanger}}{\%\ \text{Sr in solution}} \times \frac{\text{volume of solution (ml.)}}{\text{mass of exchanger (mg.)}} \qquad (5)$$

In the absence of $Cit^{3-}$, the distribution coefficient, designated as $K_d^0$, is equal to $[SrR_2]/[Sr^{++}]$, which is constant because the ratio $[Na^+]^2/[NaR]^2$ in equation (2) is constant.

We can now obtain expressions for $[Sr^{++}]$ and $[Sr(Cit)_n^{2-3n}]$ in terms of cation exchange equilibria by substitution into equation (4). The term $K_d^0$ represents the distribution coefficient of strontium when $Cit^{3-}$ is absent while $K_d$ represents the distribution coefficient when $Cit^{3-}$ is present.[2] All other conditions such as pH, ionic strength, etc., remain constant. It is also assumed here that only one complex ion is present and that the complex ion itself is not retained by the cation exchanger. Thus we have

$$K_d^0 = \frac{[SrR_2]}{[Sr^{++}]}$$

and

$$K_d = \frac{[SrR_2]}{[Sr^{++}] + [Sr(Cit)_n^{2-3n}]} \qquad (6)$$

therefore

$$[Sr^{++}] = \frac{[SrR_2]}{K_d^0} \qquad (7)$$

and

$$[Sr(Cit)_n^{2-3n}] = \frac{[SrR_2]}{K_d} - [Sr^{++}] = \frac{[SrR_2]}{K_d} - \frac{[SrR_2]}{K_d^0} \qquad (8)$$

Substitution of the expressions for $[Sr^{++}]$ and $[Sr(Cit)_n^{2-3n}]$ as given in equations (7) and (8) into equation (4) for $K_f$ leads to

$$K_f = \frac{(K_d^0/K_d) - 1}{[Cit^{3-}]^n} \qquad (9)$$

[1] A carrier-free radioactive element is one which does not have weighable or visible amounts of inactive isotopes of that element associated with it.

[2] In the general case there are as many terms in the equation for the distribution coefficient as there are molecular species containing the cation under study.

The concentration of $Cit^{3-}$ is known, and $K_d^0$ and $K_d$ are determined by measuring the fraction of tracer strontium remaining in the solution phases at equilibrium.

Equation (9) can be rewritten:

$$\log\left(\frac{K_d^0}{K_d} - 1\right) = n \log [Cit^{3-}] + \log K_f \qquad (10)$$

A plot of $\log (K_d^0/K_d - 1)$ versus $\log [Cit^{3-}]$, which can be conveniently made on log-log paper, should be a straight line with slope $n$. The value of $K_f$ is obtainable from any point on the straight line.

Equation (9) can further be arranged into

$$\frac{1}{K_d} = \frac{1}{K_d^0} + [Cit^{3-}]^n \frac{K_f}{K_d^0} \qquad (11)$$

A plot of $1/K_d$ versus $[Cit^{3-}]$ for proper values of $n$ should be a straight line which can be extrapolated to $[Cit^{3-}] = 0$ to give the value $1/K_d^0$. This procedure affords a convenient method for confirming the experimentally determined value of $K_d^0$.

## APPARATUS AND MATERIALS

*Cation Exchanger.* Any of the commercially available sulfonated polystyrene cation exchange resins can be used. These resins are particularly useful because their capacity is independent of pH over a wide range (pH $\sim$ 2–13). Air-dried Dowex-50, consisting of particles in the size range between U. S. Standard sieves, Nos. 100–140, is recommended. The size of the resin particle is not an important factor because the equilibrium distribution of the cation exchange reaction is independent of resin particle size.

The resin is conditioned by several washings, alternately with solutions of 5 per cent NaCl and 5 per cent HCl. During the conditioning process a considerable quantity of "fines" are removed. This is accomplished by stirring the resin sample in a large beaker filled with conditioning solution. Most of the resin is allowed to settle, whereupon the liquid containing the fines is decanted. This operation, when repeated several times, removes most of the "fines," hence in carrying out the equilibrium experiments, the resin settles quickly allowing the supernatant solution to be drawn off free of resin. After saturation with excess NaCl, the resin is equilibrated with excess 0.16 *M* NaCl solution. The supernatant solution in contact with the resin is adjusted to pH 7.2–7.3 with dilute NaOH solution. After the mixture has been stirred for an hour the pH of the supernatant liquid is tested, and readjusted, until no change in pH, determined with a Beckman glass electrode, takes place after stirring. The resin is filtered through a Büchner funnel, and rapidly washed free of adhering salt solution with distilled water. The washed resin is spread in a thin layer on a tray and air-dried. All experiments are conducted with air-dried resin. Analysis showed that the air-dried resin contained 3.86 milliequivalents of sodium per gram and 12.5 per cent moisture as determined by drying to constant weight at 110°C.[3] One gram of resin is required for each experiment. Enough resin in quantity sufficient for several years should be prepared and stored.

*Reagents.* Three solutions are employed: (1) a buffer solution containing $Na^+$ at a concentration of 0.16 *M* and the radioactive strontium, (2) a 0.16 *M* NaCl solution, and (3) a 0.05333 *M* sodium citrate solution. Freshly boiled distilled water is used in all solutions.

A universal Veronal[4] buffer (*4*) is employed. It contains no anions which react with alkaline earth cations to form insoluble compounds or appreciable amounts of complex ions. The buffer (pH = 7.25) is prepared as follows: 19.428 g. sodium acetate ($NaC_2H_4O_2 \cdot 3H_2O$) and 29.428 g. sodium diethylbarbiturate are dissolved in about a liter of freshly boiled distilled water. In addition 400 ml. of 8.5 per cent NaCl solution, 1100 ml. of 0.1 *M* HCl, 200 ml. of analytical reagent grade formalin as a preservative, and the carrier-free tracer $Sr^{90}$ are added[5] and the solution is diluted to five liters. The buffer solution should be kept in a refrigerator if possible.

The NaCl solution consists of 9.53 g. solid NaCl dissolved in enough water to make one liter.

For the citrate solution 15.685 g. Na citrate$\cdot 2H_2O$ (M.W. = 294.12) are dissolved in enough water to make one liter. It should be prepared fresh before each experiment, otherwise the concentration may change because of bacterial action.

*Counting Equipment.* Any device which can detect beta particles can be used for the detection and measurement of $Sr^{90}$. It is desirable but not necessary to have sufficient activity so that each ml. of the solution containing the radioactive strontium will have an activity about 100 times that of the background of the detecting instrument. The results cited below were obtained with an Eck and Krebs counter. The samples must be placed in a reproducible position beneath the tube. The samples should be counted long enough to give from 1000 total counts (3 per cent probable error) to 10,000 total counts (1 per cent probable error).

## PROCEDURE

Solutions in 12 numbered flasks are prepared as shown in Table 1. The flasks may be shaken either mechanically for at least 2 hours or intermittently by hand during a morning or afternoon. Two aliquots (the volume depending on the level of the radioactivity) are withdrawn with a pipet from the supernatant solution in each flask, and transferred to 24 numbered 10-ml.

[3] Moisture determinations are preferably conducted by drying in a vacuum oven at 40–80° or over phosphorus pentoxide in a vacuum desiccator. Oven drying at 110°C. may not give a constant weight for different kinds of resins.

[4] Veronal is a registered trade name for 5,5-diethylbarbituric acid.

[5] $Sr^{89}$ can be used if of sufficiently high specific activity, thus eliminating the necessity for allowing time for radioactive equilibrium to be attained. However, $Sr^{90}$ is readily available in the carrier-free state, is longer lived, and gives the student additional radiochemical experience.

**TABLE 1**
**Recommended Compositions of the Solutions**

| *Flask No.* | *Wt. resin, mg.* | *Strontium solution, ml.* | *NaCl solution, ml.* | *$Na_3$ Cit solution, ml.* |
|---|---|---|---|---|
| 1 | 0 | 25 | 75 | 0 |
| 2 | 0 | 25 | 75 | 0 |
| 3 | 100 | 25 | 75 | 0 |
| 4 | 100 | 25 | 75 | 0 |
| 5 | 100 | 25 | 25 | 50 |
| 6 | 100 | 25 | 25 | 50 |
| 7 | 100 | 25 | 40 | 35 |
| 8 | 100 | 25 | 40 | 35 |
| 9 | 100 | 25 | 50 | 25 |
| 10 | 100 | 25 | 50 | 25 |
| 11 | 100 | 25 | 65 | 10 |
| 12 | 100 | 25 | 65 | 10 |

flat-bottomed porcelain dishes. Care should be exercised to insure that no resin particles are transferred. To ensure a uniform deposit of salts, the solution should cover the bottom of the dish; additional water may be added if necessary.

The aliquots may be dried with an infrared bulb or hot plate or be allowed to evaporate at room temperature. Before the counting, at least 2 weeks should be allowed for reestablishment of the equilibrium between radioactive $Sr^{90}$ and its daughter $Y^{90}$.

The average activity of aliquots (1) and (2) give the original $[Sr^{++}]$ which is added to each flask, and the average activity of aliquots (3) and (4) measure the $[Sr^{++}]$ in solution after equilibrium is reached with the resin. From this $K_d^0$ can be calculated.

$$K_d^0 = \frac{[SrR_2]}{[Sr^{++}]} = \frac{[Sr^{++}]_{1,2} - [Sr^{++}]_{3,4}}{[Sr^{++}]_{3,4}} \qquad (12)$$

The activity of the last aliquots measure

$$[Sr^{++} + Sr(Cit)_n^{2-3n}]$$

for varying citrate concentration, giving the necessary data for the determination of $K_f$ and $n$ by the methods described. The accuracy of the experiment should be determined and expressed in terms of the probable error in $K_f$. Reasonable estimates of the individual probable errors of the techniques and instruments used may be substituted into the equation (*5*):

$$\frac{\Delta K_f}{K_f} = f\left(\frac{\Delta \text{ radioactivity}}{\text{radioactivity}} + \frac{\Delta \text{ concentrations}}{\text{concentrations}} + \text{etc.}\right) \qquad (13)$$

The main errors listed should include the statistical error of counting, the error in failure to obtain similar counting geometry, the error in not reaching equilibrium between $Sr^{90}$ and $Y^{90}$, and volumetric errors. Errors no greater than 5 per cent should be obtained.

**TABLE 2**
**Typical Results**

| *Group* | *log $K_f$* |
|---|---|
| 1 | 2.94 |
| 2 | 2.89 |
| 3 | 2.87 |
| 4 | 2.87 |
| 5 | 2.77 |

## TYPICAL RESULTS

Groups of students (two to a group) obtained the values shown in Table 2 for the formation quotient of strontium citrate after allowing 7 to 9 days for radiochemical equilibrium.

The values given in the literature for measurements made under the same conditions are 2.82 to 2.88 (*2*). Slightly lower results than those in Table 2 with somewhat less scattering will be observed if the samples are allowed to age the full two weeks. Corrections such as those due to complex formation by the buffer anions can be made (*2*). Additionally, the equations can be modified so as to calculate $K_f$ for positively charged complexes (*2*, *6*) and for a series of consecutive complexes such as MA, $MA_2$, $MA_3$, etc. (*6*). The effects of temperature and ionic strength on the strontium citrate complex have been determined by the ion exchange method (*1*).

## DISCUSSION

If desirable, measurements with the radioisotopes of Ca, Ba, or Ra with various organic acids can be made in place of the strontium citrate system. The weights of resin and the range in concentration of the acids would have to be modified. Another interesting variation would be the calculation of $K_f$ in systems of lower pH in which the citric acid is not completely dissociated into $Cit^{3-}$. An example of the latter situation involving calcium complexes with citric acid is available (*7*).

Other topics of interest which relate to the experiments described here are the effect of variable tracer concentrations on $K_d$ (*8*), the equilibrium theories of ion exchange (*9*), and anion exchange studies of halide complex ions of transition elements (*10*). Some of these topics, such as the limitations of the mass action expression of equation (2), can be profitably adapted for use in other student experiments in ion exchange.

## ACKNOWLEDGMENT

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# MODELS ILLUSTRATING THE LEWIS THEORY OF ACIDS AND BASES

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SINCE the Lewis concept of acidity and basicity is being used more and more in the fields of analytical and organic chemistry to account for certain experimental observations which cannot be explained satisfactorily by other theories, it seems desirable to introduce into general chemistry courses at the college level at least the rudiments of this concept. Yet few of the more widely used general chemistry texts even so much as mention the Lewis theory.

The purpose of this article is to describe a method of presenting the elements of this theory by means of cardboard models. Actually these models are nothing more than the commonly used electronic formulas in which the nucleus of the atom and all of its electrons except those of the valence shell are represented by the symbol of the element and the valence electrons by dots. It is sometimes desirable to trace the electron changes in a reaction and, for this purpose, the valence electrons of the different atoms involved are often represented by distinguishing symbols for each variety of atom rather than by dots. In this way, the transfer of an electron from one atom to another is clearly indicated and differentiation between covalent and co-ordinate covalent bonds is clearly accomplished.

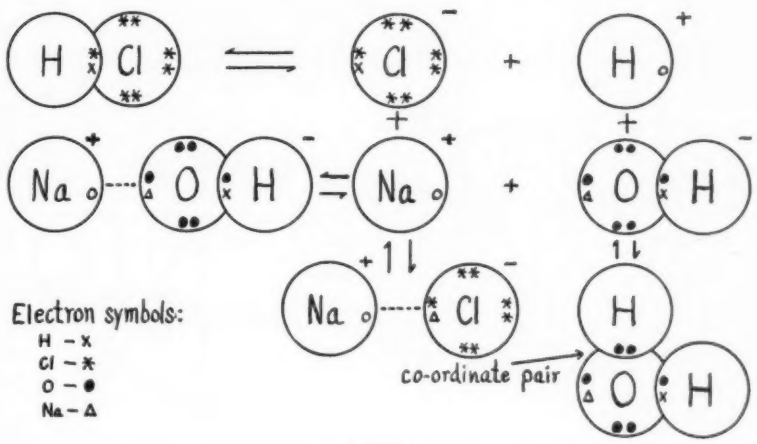


Figure 1

The models used are circular discs of white cardboard with the symbol of the element printed in large letters near the center and the valence electrons are represented by large spots near the circumference. Instead of using different symbols to distinguish between the valence electrons of different atoms as described above, the symbol and the dots representing the valence electrons are printed in a different color for each element. However, due to the fact that color printing is impossible here, differentiating symbols for electrons will be used in the illustrations accompanying this article.

In order to provide a means for joining the discs to represent ions or molecules held together by covalent or co-ordinate covalent bonds, certain of the electron spots are replaced by punched holes in which are inserted short large-headed bolts with their heads painted in the appropriate color. On other discs, holes are punched in positions not occupied by electrons in the atom of the free element but which will be occupied by shared or donated electrons when these discs are joined to represent ions or molecules. In joining the discs, the appropriate bolts are removed, the discs are lapped so that the holes coincide and the bolts are inserted in the proper holes. Where it is necessary to indicate a double bond such as that between sulfur and one of the oxygens of sulfur trioxide in Figure 4, two pairs of holes are provided to accommodate the four bolts needed and the discs consequently overlap to a greater extent. When, as in this case, the double bond is broken in the reaction, two of the bolts are moved over to the vacant holes provided for them on the oxygen disc and the oxygen and sulfur discs are reconnected in the usual manner by the remaining pair of bolts.

Covalent and co-ordinate covalent bonds are easily distinguishable here for the former will be represented by two bolt heads of different colors (different symbols in this article) and the latter by two bolt heads of the same color. Where an ion has been formed by the loss of one or more electrons from an atom, the former position of each lost electron is indicated by the vacant hole in the disc (an open circle in this article). Ions formed by gain of electrons will be distinguished by electron spots of more than one color on the disc. Admittedly, the practice of differentiating in such ways between the electrons belonging to different atoms is not strictly proper since all electrons are alike and it may lead to misunderstanding. However, this is commonly done and the disadvantages are probably outweighed by the advantages.

Figure 1 is a representation of the reaction involved in the neutralization of hydrochloric acid by sodium hydroxide according to the Arrhenius theory as com-

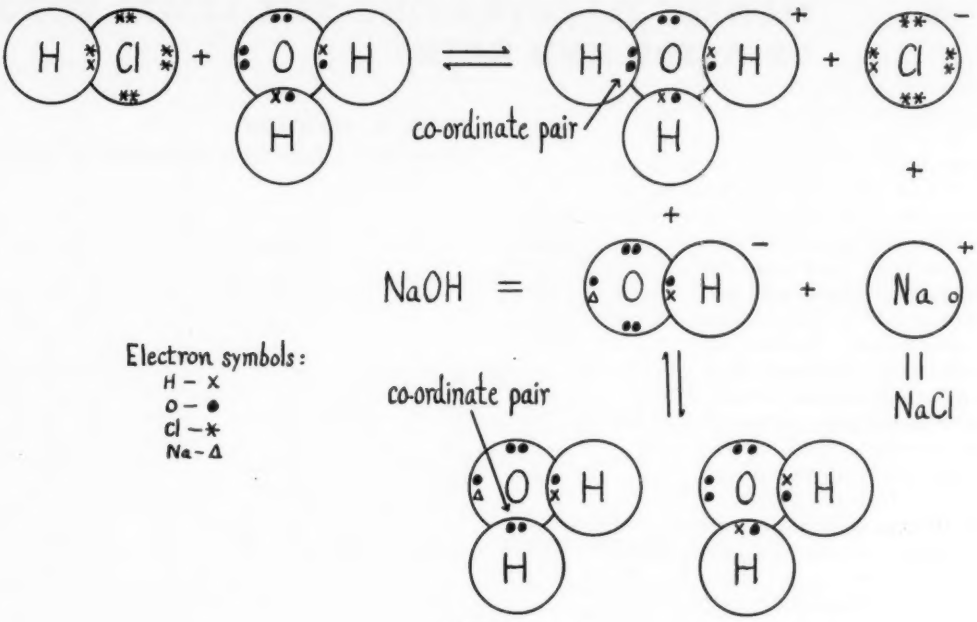


Figure 2

monly used for many years. The acid and the hydroxide are assumed to break up in solution into their ions as indicated; the electron originally belonging to the hydrogen of the acid being retained by the chlorine and that originally possessed by the sodium being retained by the hydroxyl group, thus producing charged ions. Then the hydrogen ion and the hydroxyl ion unite to form practically un-ionized water, thus causing the whole reaction to go to completion. Since the hydrogen ion has no electron either to give to or to share with the hydroxyl ion, it can unite with the latter only by accepting a share in one of the available pairs of electrons belonging to the oxygen of the hydroxyl ion. Thus we have the co-ordinate covalent bond between the hydrogen and the oxygen of the water as indicated in the figure. The sodium and chloride ions are then assumed to be attracted to each other by reason of their opposite charges.

Figure 2 represents the same reaction according to the more modern Brönsted theory. Here, water is said to be a base because it accepts proton from the acid or proton donor, hydrogen chloride. Since the proton has no electrons to share or give, it can unite with the water only by accepting a share in one of the available pairs of electrons possessed by the oxygen of the water to form hydronium ion as indicated in the figure. The hydroxyl ion of the sodium hydroxide, being a stronger base than water, can, when the solutions of hydrogen chloride and sodium hydroxide are mixed, take the proton away from the hydronium ion and, again, the proton unites with the hydroxyl ion by accepting a share in a pair of electrons belonging to the oxygen of that ion.

Solutions of hydrogen chloride and ammonia will react to form the salt-like substance ammonium chloride, the hydronium ion produced by the action of the hydrogen chloride on water combining with the hydroxyl ion produced by the interaction of ammonia and water to produce water and leaving the two ions $NH_4^+$ and $Cl^-$. These two substances will also react in the gaseous state to form ammonium chloride as indicated in Figure 3. Here, the ammonia molecule, being a stronger base than chloride ion, is able to take proton away from the latter and, again, this proton can combine with the ammonia molecule only by accepting a share in the pair of electrons possessed by the nitrogen atom of the ammonia. The resulting two ions, $NH_4^+$ and $Cl^-$ then form solid ammonium chloride.

All of these reactions are examples of the neutralization of an acid by a base to form a salt. In all of them, the base has provided a pair of electrons which it shares with a proton. This is the characteristic feature of the Lewis theory in which a base is defined as a substance which has available a pair of electrons which it can share co-ordinately with "something." In the cases cited above, that "something" was always a proton.

Figure 4 illustrates a case where the "something" which accepts the share in the pair of electrons belonging to the base is not a proton. Here, the sulfur trioxide molecule accepts a share in a pair of electrons possessed by the oxygen of the calcium oxide forming $SO_4^{--}$ ion which, together with the $Ca^{++}$ ion remaining from the calcium oxide, is equivalent to the salt calcium sulfate. Protons are not involved at all and yet there is the formation of the same salt which would be produced by the action of sulfuric acid on calcium oxide. Sulfur trioxide, according to the Brönsted definition, cannot be considered to be an acid or proton donor because it has no proton to donate. Yet it has produced

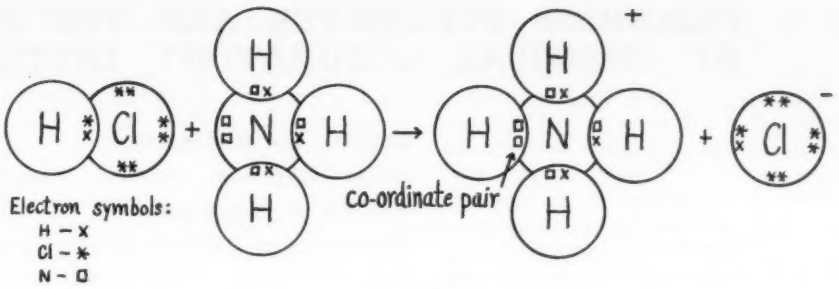


Figure 3

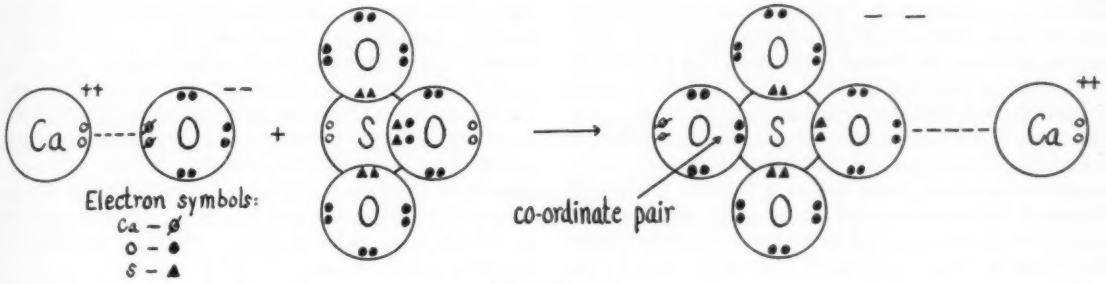


Figure 4

the same effect as an acid. The Lewis theory therefore broadens the usual conception of an acid by calling any substance which is able to accept a co-ordinate share in an electron pair an acid.

The Brönsted theory broadened the meaning of the term "base" by defining a base as anything which can accept or combine with proton. The older idea that a base is a substance which provides hydroxyl ion was superseded and it was realized that hydroxyl ion itself is a base and that substances like NaOH, which are commonly called bases, are merely carriers of hydroxyl ion, which is the actual base; the positive metallic ions have nothing to do directly with the basic properties.

The Lewis theory goes a step further. It emphasizes that the mechanism of the acceptance of proton by a base consists in the sharing of a pair of electrons, both of which are provided by the base, with the proton. It also introduces the idea that the unit which accepts the share in the electron pair need not always be a proton but may be anything capable of sharing such an electron pair, such as sulfur trioxide cited above. Also, it appears that, in the cases of hydrochloric and sulfuric acids and other substances which are commonly called acids, it is the proton provided by these substances which is really the acid, the negative ion in each case being merely a carrier of proton just as the metallic ions were seen to be merely hydroxyl ion carriers in the case of certain substances commonly called bases.

The Lewis theory, then, defines an acid as an electron pair acceptor and a base as an electron pair donor. However, in view of the fact that sulfuric acid and similar substances will probably continue to be called acids and that substances like sodium hydroxide will probably continue to be called bases, may it probably not be more practical to define an acid as an electron pair acceptor or a substance which furnishes an electron pair acceptor and a base as an electron pair donor or a substance which furnishes an electron pair donor?

# FRIEDRICH STROMEYER AND THE HISTORY OF CHEMICAL LABORATORY INSTRUCTION

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THERE is a widespread, though erroneous belief that Justus Liebig (1803–1873) founded chemical laboratory instruction when he opened a course of this kind at the University of Giessen in 1824. He himself fostered this belief; in his "Lebenserrinerungen" he wrote: "At that time, chemical laboratories in which instruction was given in analysis did not exist anywhere; what people called such, were rather kitchens, filled with all sorts of furnaces and utensils for carrying out metallurgical or pharmaceutical processes. Nobody understood how to teach analysis." Was this actually the truth?

Examination of the situation reveals that this harsh verdict by Liebig concerning the state of chemical instruction in Germany during the first quarter of the nineteenth century was not strictly correct. At that time it was possible to receive instruction in chemical laboratory practice at several German universities. Outstanding instances were: Göttingen (from 1806 under Friedrich Stromeyer); at Landshut (from 1807 under J. N. Fuchs[1]); at Jena (from 1811 under J. W. Fischer). Among these few instructional opportunities, Göttingen took a leading position, not only with respect to seniority but also because Stromeyer, along with Döbereiner, was the most eminent of these aforementioned chemists.

Friedrich S. Stromeyer was born on August 2, 1776, at Göttingen. He was the oldest son of Johann Friedrich Stromeyer, professor of medicine, and his wife Marie Magdalene, née Blum. The young man studied pharmacy at the university and so came under the influence of Johann Friedrich Gmelin (1748–1804). His studies were continued in Paris at the École Polytechnique under the eminent chemist and pharmaceutist Louis Nicolas Vauquelin (1763–1829), who as an exceptionally able analyst made important contributions to organic and inorganic chemistry and also discovered chromium (1797). Returning to Göttingen, Stromeyer took his medical degree in 1800 with a dissertation on plant geography. He then went on the usual scientific journey and visited Paris, the Pyrenees, southern France, and Switzerland. His acquaintance with such men as Vauquelin, Fourcroy, Gay-Lussac, Thenard and Dulong and their accomplishments definitely decided him to turn from medicine, a profession in which his father could have made the path to a comfortable living easy, and to devote his career to chemistry. Accordingly, in 1802 he habilitated as Privatdozent in pharmacy and chemistry. He made such a good record that after Gmelin's death, he was named extraordinary professor (1805) and then was made director of the chemical laboratory in 1806. He was promoted to ordinary professor in 1810. He later extended his teaching field into mineralogy.

The announcement of courses in those days appeared in Latin. Examination of this *Catalogus praelectionum publice et privatim in Academia Georgia Augusta* reveals that up to the winter semester of 1804–5 Gmelin offered lectures on pharmacy and also on theoretical chemistry and experimental chemistry, but no practice in analysis was offered. In the winter semester of 1805–6 Stromeyer took over the lectures in pharmacy and experimental chemistry. From the start of his teaching career he made it his guiding principle that chemistry could only be really learned through laboratory practice and that the students must be given an opportunity to carry out analyses on their own. Consequently, at this, the earliest opportunity, he also offered a laboratory course: *Privatissimis lectionibus Chemiae practicae cursum.* The same or similar offerings were made in subsequent semesters. For training in analytical chemistry he offered in the summer semester of 1810 a 3-hour lecture course: *Analyseos chemiae Laboratorio academico instituiendi.* In the following years he regularly conducted *Exercitationes chemiae practicas in Laboratorio academico,* which met one or two days each week.

Thus Göttingen, through Stromeyer, became the first German university to set up a teaching laboratory. The laboratory course was well attended and extensions and enlargements of the working space were constantly needed. The arrangements were simple, but no student got in the way of another. Those medical students who enrolled for these exercises made quantitative analyses in the laboratory and for home work were given samples which they studied qualitatively. Short papers were written about these analyses and delivered orally. Such exercises awakened an interest for chemistry among the students who

[1] PRANDTL, WILHELM, J. CHEM. EDUC., **28**, 136 (1951).
Dobereiner[2]); and at Breslau (from 1820 under N. W.
[2] PRANDTL, WILHELM, J. CHEM. EDUC., **27**, 176 (1950).

formerly had regarded this subject merely as a memory test to be reproduced for the examination.[3] The senior writer himself heard an account of this phase of Stromeyer's instructional methods and the rigid influence he exerted on his students. His maternal grandfather, Georg Katenhausen (1806–93), who was a theology student at Göttingen in his twenties, had a chemistry student among his friends. One day he found him in his room, in a highly irritable, excited mood. Before him was a chemical preparation at which he glowered. From time to time he pounded the table with his fist and then burst out: "And Stromeyer is supposed to say that I am a good enough fellow."

Stromeyer's cousin has also left an account of his lecture manner. "A powerful, agreeable voice makes his words easily understood throughout the lecture hall. Everything he says reveals the clear understanding, the certainty of his knowledge; he is an excellent teacher. He never says too much or too little; always with animation, in one lecture as in the others. His experiments never go wrong, his preciseness shows itself in the fact that he always begins and ends his lecture at the same minute, and without ever breaking the thread of his discourse. He is a model of a conscientious man of science."

The earliest practical exercises in chemistry at a German university go back two hundred years before Stromeyer, *i. e.*, to a period when "analytical chemistry," in its present sense, was not even dreamed of. In 1609 Moritz, the Landgrave of Hessia, appointed his court mathematician Johannes Hartmann (1563–1631), who had also studied medicine. to be *Professor der Chymiatrie* at the University of Marburg. Here he set up the first chemical university laboratory, in which his students also were allowed to work, but only for the making of pharmaceutical preparations, using the procedures contained in his manual: "Praxis chymiatrica." The same purpose was served also by the well-furnished chemical laboratory set up in 1683 by Johann Moritz Hofmann (1621–98) at the University of Altdorf, an institution that had been established in 1623 by the free imperial city of Nurnberg. In fact, the wet method of analysis had its beginnings with Robert Boyle (1627–91) and during the phlogistic period this branch of chemistry was developed particularly by Marggraf (1709–82) and Scheele (1742–86), and later continued by men such as Klaproth (1743–1817), Vauquelin (1763–1829) and Berzelius (1779–1848). A particularly striking testimonial to its constant development was the discovery of a large number of chemical elements. Whereas only one new elementary substance was discovered during the entire seventeenth century, namely phosphorus by Brand in 1669, the score in the eighteenth century was 20, and in the nineteenth century no less than 50 newly found elements were announced.

[3] Stromeyer, G. F. Louis, "Errinerungen eines deutschen Arztes." Hanover, 1875, pp. 124–128. The author, a noted surgeon (1804–1876), was Stromeyer's cousin.

Stromeyer himself made a valuable contribution along this line, possibly the surest way to gain chemical immortality. For years he had been making mineral analyses, with an accuracy unparalleled for his time. He tirelessly repeated his determinations until the differences in the results were eliminated. Many of these analytical studies of rocks, etc., were published and built up his reputation. In 1817, in addition to his professorship of chemistry and pharmacy, he was also named Hofrath[4] and General Inspector of Apothecaries in the entire kingdom of Hanover. His inspection visits were made according to a fixed but secret itinerary; the druggists were not told when to expect him. Under his supervision, the Hanoverian apothecaries soon ranked above those in all the rest of Germany. In spite of his strict demands the apothecaries retained a friendly attitude toward him; they remembered him with kindly sentiments, and declared "he nevertheless had a heart for us."

In 1817, while inspecting several Hildesheim pharmacies, he found that instead of the officinal "Zincum oxydatum," their stock contained zinc carbonate which, though a brilliant white preparation, on ignition produced a yellowish oxide. The material had come from a chemical factory in Salzgitter, whose director reported that this strange behavior persisted even after the most careful purification of their chemicals and that therefore his firm preferred to deliver to the apothecaries the pure white zinc carbonate rather than the yellowish oxide. On closer study, Stromeyer soon found that an unknown element was present, that it yielded a yellow precipitate on treatment of its acidified solutions with hydrogen sulfide,[5] and that it could be obtained in the metallic state by heating the brownish oxide with charcoal. Soon thereafter, Hermann, a manufacturing chemist in Schönebeck, sent him samples of yellowish zinc oxide that had been complained about by the Magdeburg pharmacists, who believed that it contained arsenic. Stromeyer confirmed his earlier findings with this material which had originated in Silesia. He named the new element *cadmium*, because of its occurrence with zinc, whose ancient name was cadmeia (*Cadmia fornacum* = tutty, which is the yellow to brown amorphous sublimate of impure zinc oxide collecting in the flues of the zinc furnaces).

Although Stromeyer liked people very much, he avoided society functions, etc., as much as possible because they made demands on his time. He consistently overworked himself. The inspection trips had to be made during the vacation periods and robbed him of the opportunity to do his own work and get the needed rest and recreation. His family life was

[4] He was thereafter referred to as the "junge Hofrath" to distinguish him from his father, the "alte Hofrath" (Privy Councillor).

[5] Stromeyer was very sensitive to hydrogen sulfide; reactions with it had to be carried out in the open. Ordinarily a most friendly person, any exposure to it in the laboratory set him wild.

happy and provided him with a substitute for social gatherings.[6]

Stromeyer was heavy-set and probably carried too much weight. In contrast, his father was slight in build and extremely active. He practiced medicine for 55 years without interruption; his son survived him only five years. Stromeyer's mental productivity decreased markedly in his later years; he had pretty much burned himself out with his incessant activities. He died of peritonitis on August 18, 1835.

Many honors came to this gifted chemist and teacher. He was elected to membership in learned societies in Göttingen, Haarlem, Berlin, Moscow, St. Petersburg, Dresden, Jena, Halle, Erlangen, Marburg, Hanover, Avignon, Frankfurt a.M., Munich, Copenhagen. Besides his numerous papers, which dealt principally with analyses of minerals and which for the most part appeared in the *Transactions* of the Göttingen Societät der Wissenschaften and *Schweigger's Journal*, he also published (at Göttingen): "Tabellarische Übersicht der chemisch einfachen und zusammengegesetzten Stoffe" (1806); "Grundriss der theoretischen Chemie" (1808); "Untersuchung über die Mischung der Mineralkörper und anderer damit verwandter Substanzen" (1822).

If the young Liebig, in the fall of 1820, had not gone to Bonn to study under Kastner[7], but instead had enrolled at Göttingen under Stromeyer, he would certainly have received an excellent training in analytical chemistry, and in after years would have had no reason to complain so bitterly about the state of academic instruction in chemistry in Germany. Although Stromeyer did not have the honor of including Liebig among those who were indebted to him for their basic chemical training, he nevertheless did teach two others who later brought great credit to him through their brilliant careers. They were Mitscherlich and Bunsen.

Eilhard Mitscherlich (1794–1863) came to Göttingen, not really to study chemistry, but because he was intensely interested in Oriental languages, and his uncle, the eminent philologist C. W. Mitscherlich was professor there. Previously, the young Mitscherlich had been studying in Heidelberg (1811) and then in Paris (1813) and had hoped that he would be chosen as a member of the legation, which Napoleon was planning to send to Persia. When this plan fell through because of Napoleon's defeat at Leipzig (October, 1813), Mitscherlich decided to study medicine so that he could perhaps get to the Orient as a ship's doctor. As a beginning medical student he attended Stromeyer's lectures and worked in his laboratory. The latter sensed the young man's special aptitude in chemistry and persuaded him to change from medicine to chemistry, though he took his doctorate with a dissertation on Persian poetry. Chemists know full well the successes of Mitscherlich as a chemist and teacher.[8]

The second Stromeyer pupil, who achieved world-wide distinction in chemistry, was Robert Wilhelm Bunsen (1811–99). Bunsen, a native of Göttingen, where his father was both professor and university librarian, started his higher training there in 1828 and took all the available work that dealt with natural science, including of course Stromeyer's offerings. Bunsen's doctoral dissertation (1831) contained nothing chemical. It bore the high-sounding title *"Enumeratio ac descriptio hygrometrorum, quae inde a Saussurii temporibus proposita sunt."* This compilation of descriptions of hygrometers that had been proposed since Saussure (1740–99), bore a dedication to his highly respected teacher: *"Viro illustrissimo excellentissimo naturae scrutatori sagacissimo praeceptori pie colendo Friderico Stromeyer."* As Privatdozent, it became Bunsen's task to give the large chemistry lectures and to conduct the student laboratory after Stromeyer's death in August 1835. This arrangement continued until the next spring, when Stromeyer's successor, Friedrich Wöhler, took charge. Bunsen then went to Cassel, where he took Wöhler's place at the Gewerbeschule.[9]

Although Stromeyer must be given the credit for being the first to have offered practical courses in chemical analysis in German universities, this priority in no way detracts from the extraordinary service rendered to chemical education by Liebig, who must still be regarded as the founder of the modern chemical curriculum, with its insistence on laboratory practice.

[6] His wife was the widow of his close friend Dr. Röhden. Their three daughters had sunny dispositions and the oldest was known as "the star of Göttingen" because of her outstanding personality. Their only son, Eduard Christian Friedrich (*b.* 1807) took his medical degree at Göttingen in 1831 and was made professor of medicine in 1836.

[7] OESPER, R. E., J. CHEM. EDUC., **4**, 1461 (1927).

[8] WINDERLICH, R., J. CHEM. EDUC., **26**, 358 (1949).

[9] For details of Bunsen's life and works see LOCKEMANN, G., "Robert Wilhelm Bunsen," Stuttgart, 1949; OESPER, R. E., J. CHEM. EDUC., **4**, 431 (1927).

# FOURTH ANNUAL CONFERENCE ON THE TEACHING OF COLLEGE CHEMISTRY

## WESTERN BRANCH

Pasadena, California

THE Western Branch of the Fourth Annual Conference on the Teaching of General Chemistry, under the title of General Chemistry Workshop, will be held at the California Institute of Technology, Pasadena, California, during the period June 22–29, 1953, inclusive. This workshop is sponsored by the Division of Chemical Education of the American Chemical Society.

The morning sessions will be devoted to formal lectures, with discussion, and to special activities. The afternoon sessions will be in conference groups of the participants' choice. Special attention will be paid to the problems of the teachers of chemistry in the junior colleges. Organization of these study groups will take place on the first day. The study groups will be directed by Dr. T. Bentley Edwards.

### DIRECTORS

Dr. Linus Pauling is Professor of Chemistry, Chairman of the Division of Chemistry and Chemical Engineering, and Director of the Gates and Crellin Laboratories of Chemistry at the California Institute of Technology. He has taught courses in general chemistry during the major part of his professional life. He is author of the books "General Chemistry," "College Chemistry," "The Nature of the Chemical Bond," "The Structure of Line Spectra" (with S. Goudsmit), and "Introduction to Quantum Mechanics" (with E. B. Wilson, Jr.).

Dr. T. Bentley Edwards, Director of the Workshop sessions, received his Ph.D. from the University of California. His teaching experience includes service as Associate Professor and Head of the Chemistry Department, St. Mary's College, and his present position is Assistant Professor of Physical Science, Chico State College, Chico, California. He is coauthor of "Science and Life" and "Science and Progress."

Dr. Harper W. Frantz received his Ph.D. degree at the University of California in 1927. For many years he taught chemistry at LaVerne College, and at present he is Professor of Chemistry at Pasadena City College. He is author of "A Laboratory Study of Chemical Principles" and, with Lloyd E. Malm, of "College Chemistry in the Laboratory" and "A Laboratory Course for Pauling's General Chemistry."

Dr. Norman Davison is Associate Professor of chemistry at the California Institute of Technology. He studied as a Rhodes scholar at Oxford University, and received his Ph.D. at the University of Chicago in 1941.

### INVITED SPEAKERS

Dr. Richard E. Powell, Associate Professor of Chemistry, University of California at Berkeley, and co-author with Joel Hildebrand of "Principles of Chemistry," and with W. C. Bray and Wendell M. Latimer of "A Course in General Chemistry," will speak on demonstrations in the teaching of general chemistry.

Dr. O. Meredith Wilson, Secretary of the Fund for the Advancement of Education established by the Ford Foundation will discuss the work of the Fund, with special emphasis on the parts of the work of interest to teachers of chemistry.

Dr. Karol J. Mysels, Associate Professor of Chemistry at the University of Southern California, and co-author with C. S. Copeland of "Introduction to the Science of Chemistry," will discuss the teaching of the concept of equilibrium in the first-year chemistry course.

Dr. Ernest H. Swift, Professor of Analytical Chemistry, in the California Institute of Technology, will speak on the function of qualitative analysis in the general chemistry course. He is the author of the books "Introductory Quantitative Analysis" and "A System of Chemical Analysis for the Common Elements," and co-author with Arthur A. Noyes of "A Course of Instruction in Qualitative Chemical Analysis of Inorganic Substances."

Dr. Harrison Brown, Professor of Geochemistry at the California Institute of Technology, will discuss the subject of geochemistry.

### INFORMATION

The registration fee will be $10.

Participants in the General Chemistry Workshop can be accommodated in private rooms in the student houses on the campus of the California Institute of Technology at 1201 East California Street, Pasadena, California. The rates are $3.50 per night, or $17.00 per week (maximum 7 nights). Married couples can be accommodated in one room with two beds at double the individual rate. Bathroom facilities are available on each floor. The guests will reside in Fleming House, and the lounge will be available for informal social gatherings.

More luxurious accommodations, with private bath, can be obtained at the Constance Hotel, 940 East Colorado Street, Pasadena, which is about 3/4 mile from the campus.

Requests for reservations in the student houses should be addressed to Professor Linus Pauling, Cali-

fornia Institute of Technology, Pasadena 4, California, and for hotel reservations to the hotel. It is requested that reservations be made well in advance of the meeting.

Meals can be obtained by participants in the workshop at the Athenaeum (the faculty club of the California Institute of Technology) and at the Coffee Shop. Both the Athenaeum and the Coffee Shop are close by the student houses.

The workshop meetings will be held in the Gates and Crellin Laboratories of Chemistry, on the campus of the California Institute of Technology.

## EASTERN BRANCH

### State College, Pennsylvania

THE Eastern Branch of the Fourth Annual Conference on the Teaching of College Chemistry will be held at Pennsylvania State College, June 10–19, 1953.

#### GENERAL CHEMISTRY WORKSHOP

The Directors: Dr. Grant W. Smith, Professor and Director of General Chemistry at Penn State College, has had 16 years of experienced teaching. In addition he has taught at Itasca Junior College (Minnesota), Crinnell College, University of Kansas City, and the University of North Dakota where he was head of the Department of Chemistry. He is chairman of the committee which recently prefaced the "Handbook for Chemistry Assistants."

Dr. W. Conrad Fernelius, Professor and Head, Department of Chemistry, Pennsylvania State College.

#### ANALYTICAL CHEMISTRY WORKSHOP

The Second Annual Conference on Analytical Chemistry is to be held June 10–19 concurrently with the General Chemistry Workshop, but the two groups will operate independently. Organization of work groups will be made at the first general session on June 10.

The Director: Dr. Edward Haenisch has had 18 years of experience teaching and research in the field of analytical and physical chemistry. He is author of "Quantitative Analysis" (with W. C. Pierce); his present position is Professor and Chairman of the Department of Chemistry, Wabash College, Crawfordsville, Indiana.

#### INFORMATION

The formal lectures will be confined to several short morning sessions. It is planned to include lectures by recognized authorities on the following subjects: (1) Safety in the chemistry laboratory (2) Lecture and classroom demonstrations (3) Instructional films in chemistry (4) Special topics of interest to teachers of general and analytical chemistry.

State College may be reached via Pennsylvania Rail Road (Lewiston) and thence by bus. The registration fee will be $15. Those desiring 2 semester hours of graduate credit may register with an additional fee of $3.

Rooms in the college dormitories located on the campus will be available at the rate of $2 per day per person. Married couples with or without children can be accommodated. Meals served in the dining commons near the dormitories are available at about $3 per day.

The location of Pennsylvania State College in the mountains offers unusual opportunities for golf, tennis, swimming, hiking, and fishing for registrants and their families.

Requests for reservations and information should be addressed to Dr. Grant W. Smith, Department of Chemistry, The Pennsylvania State College, State College, Pennsylvania.

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THE following, a mnemonic aid for the actinide series, is contributed by Ervin Colton of the University of Illinois. It is a companion to the one for the rare earth series which appeared in a past issue [J. CHEM. EDUC., **28**, 372 (1951)]. The symbols of the elements are italicized.

*Actual thoughts pass under Neptune's public amnesty, calming balky coffles.*

*Report of the*

NEW ENGLAND ASSOCIATION OF CHEMISTRY TEACHERS

# EVALUATION OF LABORATORY WORK IN GENERAL CHEMISTRY[1]

**ARNOLD J. CURRIER**
Pennsylvania State College, State College, Pennsylvania

INDIVIDUAL laboratory work is now regarded as a vital part of the teaching of general chemistry in colleges and universities. The student will naturally be expected to do better work if he knows that he will be given proper credit for his efforts. Evaluation of the laboratory work of the student is a complex problem especially in the larger institutions where the work is handled largely by graduate assistants with little or no experience.

The objectives of the laboratory work in a given course must naturally be taken into consideration in determining what criteria are to be used in the evaluation of the work. As a practical statement, it would seem that the main objective is to give the student experience in working with substances under guidance. In other words, to learn chemistry by "doing chemistry." Schlesinger (*1*) has clearly stated other important objectives, *viz.*, to train the student to observe, to think and to act. To devise experiments and tests in conformity with these objectives is a challenge to the industry and ingenuity of every teacher.

It is the major purpose of this paper to consider some of the items involved in evaluating student laboratory work, particularly with regard to current practice in the colleges of New England and Pennsylvania.

To obtain information on evaluation of laboratory work, a questionnaire was sent in March, 1952, to 38 members of the New England Association of Chemistry Teachers in the colleges and universities. Data were requested on the percentages of credit given to six aspects of the student's work: completeness, independence, technique, quizzes, notebooks or reports, and "unknowns." Information was also requested on the number of courses given and the type of notebook or report used.

Of the 26 (68 per cent) of the questionnaires returned, 18 did not report specific percentages, allocated to the various items, in determining the grade for the laboratory work. In these colleges, it is presumed that a composite laboratory grade is given which is based upon the general observation and judgment of the instructor. Several instructors indicated that the relative percentages varied from week to week.

A smaller number (8) of the questionnaires reported specific percentages for most of the items listed. Data from this group are summarized in Table 1.

The same questionnaire was distributed at the first meeting of the Pennsylvania Conference of College Chemistry Teachers (PCCCT) in April, at State College, Pennsylvania. Of the 12 institutions reported, 8 indicated specific percentages of credit allocated to most of the items as shown in Table 1.

**TABLE 1**

| *Items given special credit* | | *Number of colleges reporting percentages* | *Percentage of credit given* Minimum | Maximum |
|---|---|---|---|---|
| Completeness | NEACT | 4 | 10 | 20 |
| | PCCCT | 3 | 10 | 15 |
| Independence | NEACT | 4 | 17 | 40 |
| | PCCCT | 2 | 10 | 15 |
| Technique | NEACT | 5 | 10 | 50 |
| | PCCCT | 5 | 10 | 33 |
| Quizzes | NEACT | 5 | 10 | 100 |
| | PCCCT | 7 | 12 | 80 |
| Notebook or report | NEACT | 5 | 15 | 50 |
| | PCCCT | 4 | 10 | 33 |
| Unknowns | NEACT | 5 | 10 | 33 |
| | PCCCT | 6 | 5 | 30 |

Data concerning the number of courses given and the type of notebook or report used are presented in Table 2.

Although the number of institutions reported is rather limited it should be emphasized that many of them have large enrollments. The data, therefore, present a fairly comprehensive "picture" of current practice in the areas reported. It is of interest to note the wide variation in the percentage of credit given to the various phases of laboratory work. For example,

[1] Presented as part of a symposium at the Fourteenth Summer Conference of the NEACT, University of Vermont, Burlington, Vermont, August 22, 1952. Andrew J. Scarlett, Dartmouth College and Carl P. Swinnerton, Pomfret School, also contributed to this symposium.

**TABLE 2**

| *Number of courses* | *Type of notebook* |
|---|---|
| NEACT | |
| 1 course in 8 colleges | Blank book form in 13 colleges |
| 2 courses in 10 colleges | "Fill in" form in 13 colleges |
| 3 courses in 6 colleges | |
| 4 courses in 2 colleges | |
| PCCCT | |
| 1 course in 4 colleges | Blank book form in 6 colleges |
| 2 courses in 8 colleges | "Fill in" form in 6 colleges |

the percentages for quizzes (oral and written) varies from 10 to 100 per cent and the percentage for notebooks or reports varies from 10 to 50 per cent.

Amplifying statements in the questionnaires show a recurring emphasis upon the value and importance of the oral and written quiz and a diminishing emphasis upon notebooks and reports. Some instructors stated that the longer "essay type" of report is of considerable value to the student, when it is done under proper conditions.

One teacher reported that 100 per cent of the laboratory grade is based upon quizzes; ". . . 10 quizzes per semester marked on a basis of 10 credits each. The quiz is on the previous week's laboratory work and is given at the beginning of the laboratory period (approximately 20 minutes). Laboratory grade counts $^1/_4$ of the course grade."

Another teacher made the following comments: "Too many students relay on fraternity files for their formal reports. The laboratory examination tends to 'square things up'. . . . My experience with 'fill in' sheets and blank page notebooks has not been satisfactory; too much is written in before the experiment is performed. Often, very little actual work is done in the laboratory and the report is turned in containing only 'textbook observations.' I wish I knew some really good way to make students think and learn in the laboratory."

**TABLE 3**

| *Type of college* | *% Wt. of lab. grade in course grade* | *Note book, %* | *Observance of performance, %* | *Oral quiz, %* | *Written quiz, %* | *Misc. %* |
|---|---|---|---|---|---|---|
| Liberal arts | 29 | 32 | 29 | 12 | 23 | 4 |
| University | 26 | 38 | 19 | 6 | 34 | 3 |
| Sci. eng., agr., and technical | 30 | 30 | 30 | 18 | 22 | 0 |
| Approximate averages | 28 | 33 | 26 | 12 | 26 | 2 |

**TABLE 4**

| *Item* | *Chem. 1 5 credits, %* | *Chem. 3 3 credits, %* | *Chem. 2 5 credits, %* | *Chem. 4 3 credits, %* |
|---|---|---|---|---|
| General lab. performance | 33 | 33 | 20 | 20 |
| Notebooks | 33 | 33 | 20 | 20 |
| Quizzes | 33 | 33 | 20 | 20 |
| Unknowns | | | 40 | 40 |

A partial answer to the problem presented in the previous quotation is proposed by another teacher in the following statement: "We do not require any outside work on reports. Students come to the laboratory, do their work, check it with the instructor, and that constitutes their final responsibility on each exercise. After trying to have written reports prepared outside, for grading, we came to the conclusion that we were wasting our time and so were the students. We try to make the principle behind the exercise the most important item, second, the method of obtaining information about that principle (*i. e.*, techniques). While this attitude does allow the uninterested student to 'get away' with less work than a complicated system of report writing and grading would do, we are satisfied that it is best for us."

Another comment by still another teacher is significant: "The close association of each student, during laboratory time, with the instructor who is not afraid to get foot weary, has not only much teaching opportunity, but also gives the instructor much information not found by other means. Some way of evaluating this information might be sought."

To eliminate some of the common undesirable practices in laboratory work, *e. g.*, copying of laboratory notes from other reports or from nearby students, "cookbook" or unintelligent following of instructions, etc., Secrist (*2*) offers constructive suggestions based upon the procedure used in his laboratory. In place of the usual laboratory report, the students take a short written quiz during the last 15 minutes of the laboratory period, covering the experimental work just completed. Some of the advantages named by Secrist are: (*a*) a more serious and thoughtful attitude of the student toward the laboratory work, (*b*) the tendency to leave the laboratory early is discouraged, (*c*) the laboratory desks are cleaned more carefully so as to be in good condition for writing the quiz, (*d*) a minimum of time is required for grading the quizzes—probably less than the time used in grading laboratory reports, (*e*) the grades on the tests are generally good and serve to maintain interest in the laboratory work.

A more extensive survey of the evaluation problem was conducted by C. S. Adams (*3*) in 1942, in which a questionnaire was sent to 175 colleges and universities. Replies were received from 140 institutions in 46 states. The information thus obtained is summarized in Table 3.

From the approximate averages in Table 3 it is evident that rather high percentages were allocated to quizzes (12 + 26, or 38 per cent) and to notebooks (33 per cent). The observation of performance also rated 26 per cent.

A tentative plan for grading laboratory work at the Pennsylvania State College is shown in Table 4.

General laboratory performance covers care of desk and reagents, manipulative skill and technique, initiative, punctuality, and understanding of the work done. Notebooks or reports are graded on a scale of 10 as follows: 9 to 10, Superior; 6 to 9, Satisfactory; below 6, Unsatisfactory.

From our recent discussions and from the comments of a number of instructors who reported on the questionnaire, it appears that a decreasing emphasis is placed upon the student's notebook or written report. Although we do recognize the importance of checking errors or misconceptions, the notebook, it seems, is to be regarded as the student's own project which is to serve in helping him to "crystallize" the first hand knowledge which he has acquired from his experimental work.

The preparation and the relative merits of the various types of written tests for laboratory work is beyond the scope of this paper. We have experimented with objective laboratory tests on a limited scale with good results and plan to do further work. A typical question was stated as follows:

A substance was observed to react with water, forming a solution which turned red litmus blue and a gas which burned. Check below the correct conclusion from this experiment.

( ) 1. Calcium hydroxide and acetylene were formed.
( ) 2. A base and a hydrocarbon were formed.
( ) 3. Sodium hydroxide and hydrogen were formed.
( ) 4. Calcium hydroxide and hydrogen were formed.
( ) 5. A base and a combustible gas were formed.

Engelhart (*4*) has contributed a very practical and extensive discussion of objective tests in chemistry which should be very helpful to teachers who desire to improve their testing procedures.

Hendricks (*5*) describes laboratory tests in which the student is asked to set up and perform experiments under the direct observation of the instructor. Apparently, this type of test requires experienced instructors, considerable time, and small classes to insure satisfactory results.

## SUMMARY

(1) The large institutions, in general, reported that a percentage rating of the various items (quizzes, notebooks, unknowns, etc.) is used in determining the laboratory grade. There is a wide variation in the relative percentages assigned to these items.

(2) The smaller institutions, in general, reported that a subjective and conposite rating is the basis for the laboratory grade.

(3) Decreasing emphasis is placed upon the student's notebook as a basis for laboratory grades in both the larger and the smaller institutions.

## ACKNOWLEDGMENT

The author wishes to express appreciation to the many individuals for their cooperation in the preparation of this report. The college teachers in New England and Pennsylvania have added many constructive comments in their replies to the questionnaire. The committee on laboratory work at the first conference and workshop in General Chemistry (Oklahoma Agricultural and Mechanical College, June, 1950), of which the author was a member, emphasized the objectives stated in this paper. Grant W. Smith, Director of General Chemistry, Pennsylvania State College, has made helpful suggestions and, last year, appointed the following committee on evaluation of laboratory work: Herman H. Appledorn, Warren W. Miller, Thomas Wartik, and Arnold J. Currier, Chairman. Some of the material of this paper has been worked out by this committee. The criticisms of the general chemistry staff have been most helpful.

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*To the Editor:*

In connection with the article, "A demonstration on the chemistry of color," by Stanley C. Bunce and Henry F. Hammer [J. CHEM. EDUC., **28**, 546 (1951)], I should like to call attention to an easily-conducted and significant experiment, the *complete* removal of a dye from solution. For this purpose the acid dye Crystal Ponceau (Ponceau 6R, prepared from 1-naphthylamine and 2-naphthol-6-8-disulfonic acid) is well adapted. Proceed as follows: Add a few drops of acetic acid to 5 ml. of the dye solution (0.05 per cent) in a test tube, introduce 0.1 g. of white wool yarn, and set the test tube in a boiling water bath. After 20 to 30 minutes the solution should be entirely colorless.

Concerning the "Experiment on the law of multiple proportions," by John H. Secrist [J. CHEM. EDUC., **29**, 283 (1952)], I should like to observe that according to my experience results with impure $Cu_2O$ are entirely

unsatisfactory. It would have been helpful if the author had given the analytical data for the preparations which he used. The German literature contains directions for purification, for example by R. Scharf [*Z. physik. chem. Unterricht*, **47**, 202 (1934)]. A still better purification method has been developed by L. Doermer, which will appear in the new (6th) edition of "Technik der Experimentalchemie."

WALFRIED SEEGER

BUNDESREALSCHULE
DORNBIRN, AUSTRIA

*To the Editor:*

Lecture demonstrations are extremely effective teaching devices. Indeed, their pedagogical soundness is hardly debatable. As Dr. Rakestraw once said of the practice: "I can scarcely imagine proceeding without it." I don't suppose a single teacher exists who does not use demonstrations in his teaching. In some setups a vast array of demonstration equipment is available and special staff is on hand to set it up. Now what happens? The *usual* procedure is well known. The experiment is set up, either by the teacher himself or by his demonstrator, and wheeled into the classroom. With a semblance of drama the routine is run through. (Note, please, that this drama is a very necessary ingredient and too few teachers possess it!) The instructor gives some discussion appropriate to the experiment, *sometimes* asks if there are any questions (this invariably not often enough), turns to the blackboard and takes up his lecture. The bell rings, the class goes, the equipment disappears. The episode is closed. Only rarely does any discussion ensue among the observers. It is reasonably safe to say that little of the experiment was understood by the majority of the students. How do I know? I have asked students to explain or describe to me what went on, and why it did, and I find they can't! If the demonstration is exciting or intrinsically dramatic the student is entranced and he goes away with great wonder, but this is no guarantee that he is instructed. Can we improve this situation?

For several years I have resorted to a scheme in physics which has shown itself to be instructionally sound. I believe the device can be profitably used by chemistry teachers. *I require the student to write up the demonstration experiment.* This he does in a bound notebook reserved for these write-ups alone. He gives it a title; he recites the procedure in his own words; he describes what was done, what happened, and why. Some students do an astonishing job; some give an historical comment, if one is appropriate; some carry the experiment to interesting extensions. But in general the write-ups are shamefully inadequate. Most of the people do not know what was going on! Apart from this, the linguistic performance is astonishing. Students cannot write acceptable English. This device, then, is good practice—a practice sorely needed.

I read the reports critically. This is a chore and a travail. But it is informative to find how much (or more often, how little) of what I said and did took root. By this device the *student* has exercise in formal exposition. *I* learn how to improve my demonstrations.

Obviously, the student is now under compulsion to watch the demonstration critically, and when he writes it up some critical thinking is demanded.

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## INTRODUCTION TO THE STUDY OF PHYSICAL CHEMISTRY

***Louis P. Hammett,*** **Professor of Chemistry, Columbia University. McGraw-Hill Book Co., Inc., New York, 1952. xii + 427 pp. Illustrated. 16 × 23.5 cm. $6.**

IN HIS "Foreword to the Student of Physical Chemistry" at the beginning of this book, Professor Hammett says: "In a world in which there is so much that is interesting to be learned I have tried to avoid wasting your time by repeating things you should have learned in your previous studies." In adhering to this policy, the author has omitted a good deal of material which is found in most other textbooks on this subject. For example, Faraday's laws of electrolysis, which occupy at least a page, and usually more, in most texts, are given one sentence here (page 204): "By Faraday's *laws of electrolysis* (Pauling 303, Timm 342) the ratio of the quantity of electricity transferred to the quantity of chemical change is the constant quantity, 96,493 coulombs/equiv. (23,062 cal./volt-equiv.) regardless of the reaction involved." For the student who wants to refresh his memory, references to standard texts in chemistry (such as those of Pauling and of Timm mentioned in this connection), physics, or mathematics are scattered throughout the book.

Crystal structure is not discussed, since it is almost always treated in an elementary manner in general chemistry or physics

or both, and "the three-dimensional geometry and optical theory involved in the actual interpretation of x-ray diffraction data is so involved that it can be understood only by an effort much too great for inclusion within the bounds of the present undertaking." Atomic structure is omitted for similar reasons. Although a brief chapter on surface effects is included at the end of the book, no mention is made of colloids. Colligative properties of solutions are not mentioned as such, but Raoult's law is presented adequately, and the equations for freezing-point depression, boiling-point elevation, and osmotic pressure are derived; the student is apparently expected to be familiar with descriptive aspects of these phenomena from his earlier study.

The first law of thermodynamics and the principles and applications of thermochemistry are presented in conventional fashion, but the treatment of the second law and its consequences is unusual for a textbook at this level. The first five chapters of the book take up gases, kinetic theory, solutions, the first law, and thermochemistry, and they are not very different from similar chapters in many other books except that much material which should have been learned earlier is omitted. Chapter six is entitled An Elementary Discussion of Quantum Principles and the Use of the Boltzmann Equation, and much of what follows is based on this chapter.

Chapter seven, entitled The Ideal Law of Chemical Equilibrium begins with a very brief discussion of the second law in terms of the existence of a state of equilibrium toward which all systems tend to change, and this is followed by a detailed discussion of equilibrium constants in ideal systems. The student is reminded of the derivation of the equilibrium constant given in general chemistry courses, but no more exact derivation is given here. In the next chapter, the Boltzmann equation is used to interpret the condition of equilibrium between isobutane and normal butane, and this is related to the equilibrium constant. Then the "partition function" is introduced, and its applications to equilibrium and especially to the effect of temperature on equilibrium are considered in detail. The standard free energy is then defined, in terms of partition functions, and standard entropy is likewise defined and used, but one wonders whether at this stage these concepts will have any concrete meaning for the student—although admittedly even the more traditional treatment leaves many students with only the haziest notion of entropy and perhaps not an altogether clear idea of the significance of free energy.

Although this statistical approach to chemical problems is sound enough, there is some doubt in this reviewer's mind whether it is a satisfactory way to teach the subject to college undergraduates. Most students in the course for which this text is designed will have had mathematics only through a year of calculus, and for them several gaps must be left in the derivations; when the more traditional thermodynamic approach is used, such gaps need not be left, since no mathematics more advanced than partial derivatives is needed. To make clear the significance of the partition function at this stage may involve a greater expenditure of time than is warranted. On the other hand, statistical methods are becoming more and more important in physical chemistry, and it might well be argued that this is the place to begin using them. Whether or not teachers of physical chemistry are prepared to abandon more traditional methods in favor of this, they would do well to consider carefully this point of view. No halfway acceptance seems possible, since the book is internally consistent, and such concepts as the partition function are used frequently once they have been introduced. A teacher could hardly expect his students to use this text consistently unless he were willing to abandon the more familiar point of view in his classroom presentation.

The next chapter deals with reaction kinetics; although the first part of the chapter can be understood without what has gone before, in the latter part statistical mechanical methods are fundamental to the discussion. In the succeeding chapter, on galvanic cells, potential difference at an electrode is presented in these terms, but the remainder of the chapter is rather conventional.

In the next chapter, thermodynamics is applied to chemical problems through the concepts of reversible work, useful work, free energy, and chemical potential. The discussion of free-energy change as a criterion for equilibrium is especially good. These ideas are then used in connection with nonideal systems.

The chapter on phase diagrams begins with an unusually clear introduction to the phase rule; the rest of the chapter discusses phase diagrams of systems of various types. This is followed by a chapter on conductance which is sound but not unusual.

The next chapter is entitled Special Properties of Chemical Reactions in Ionic Solutions, and, as might be expected in view of the author's previous writings, it is well and clearly done. It is followed by a chapter entitled The Effects of Pressure and of Temperature on Free Energy, which includes a number of important topics, such as a definition of temperature, the Gibbs-Helmholtz equation, the Clausius-Clapeyron equation, and a brief quantitative treatment of osmotic pressure. This chapter is somewhat disjointed; the topics might well have been incorporated into earlier chapters.

The last chapter in the book discusses a few surface effects, including absorption and catalysis. There are two appendixes, the first explaining in detail some of the mathematical techniques commonly used in physical chemistry, and the second relating the Boltzmann equation to probability considerations.

In the foreword, the author states his opinion that "the problems are the most important part of a book of this sort, and what you will have learned from the study of this text will be measured by the quality of the intellectual effort provided for you by the problems and by your willingness to make the effort." Each chapter concludes with searching and stimulating problems ranging in number from 7 to 31, and averaging about 16.

One of the best aspects of this book is the care which the author takes to present physical chemistry as a growing science, in which conclusions are not necessarily final, and to point out clearly what has not been proved, as well as what has. For example, after discussing the study of the bromination of acetone and presenting a possible mechanism for the reaction, he says (page 179): "This tool (i. e., the study of reaction rates) does not often give an unambiguous positive answer; it rarely says, 'This is the mechanism.' But it frequently says unambiguously, 'This is not the mechanism,' and the conclusion is important even though sometimes unpalatable."

The book is stimulatingly different from other texts in this subject; whether or not a teacher feels that he can use it effectively as the one required text for his course, he can profit greatly from its point of view. And if he is willing to take the time to help his students to overcome the basic difficulties of some of the ideas on which further developments are based, he may find it a thoroughly satisfactory text.

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## ● ANNUAL REVIEW OF PHYSICAL CHEMISTRY. VOLUME III

***G. K. Rollefson,*** **Editor, and** ***R. E. Powell,*** **Associate Editor, both of the University of California. Annual Reviews, Inc., Stanford, Calif., 1952. ix + 416 pp. 15 figs. 12 tables. 16 × 23 cm. $6.**

IT HAS become trite to say that science has grown so complex and specialized that no individual can hope to be competent outside of his own particular field. A hasty thumbing through of one volume of these "Annual Reviews" is enough to convince one that even the relatively small part of science known as physical chemistry is more than can be mastered by any individual.

This series, of which the present volume is the third, is an attempt to present up-to-date accounts of advances in physical chemistry, and is well on its way to becoming one of the most useful publications available to teachers and research workers in this field. The editors have succeeded in persuading several of our most competent scientists to review recent contributions in their various specialties.

In the present volume, 19 topics are discussed, 16 of which were

treated in last year's volume, three of which are new. The new subjects are: "Bond energies and bond distances," "Polarography and electrode processes," and "Theory of ionic crystals, semiconductors, and dielectrics." The others are: "Quantum theory, theory of molecular structure and valence," "Radioactivity and nuclear theory," "Isotopes," "Radiation chemistry," "Polymeric electrolytes," "Ion exchange," "Thermochemistry and the thermodynamic properties of substances," "Heterogeneous equilibria and phase diagrams," "Photochemistry," "Photosynthesis," "Spectroscopy," "Solutions of nonelectrolytes," "Solutions of electrolytes," "Reaction kinetics," "Experimental crystallography," and "Experimental molecular structure." The topics from last year which were omitted this year will be largely covered in next year's volume. It is apparently the policy of the editors to ask different people to review a particular subject in different years, since none of last year's contributors is represented in this volume, and none from this year's is scheduled for next. The treatment of the various topics is very uneven; some chapters (of which that on thermochemistry is an example) are little more than listings of references, while others (such as "Solutions of electrolytes") are critical and somewhat detailed presentations of recent developments, with a good deal of background material. Some of the authors have tried to cover the whole field of the assigned topic, while others have quite frankly confined themselves to those parts of the subject in which they are especially interested. For example, the chapter on "Heterogeneous equilibria and phase diagrams" is limited to advances in mineralogical and ceramic systems.

As might be expected, some of the topics are more interesting and of more value than others to the general reader. No chemist, however, can fail to profit by something in this book, and any physical chemist who is interested in research will find it, as well as the two preceding volumes, highly valuable. There is every reason to anticipate that succeeding volumes will continue to bring to scientific workers useful accounts of significant advances in physical chemistry.

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## ● STATISTICAL THEORY WITH ENGINEERING APPLICATIONS

***A. Hald,*** **Professor of Statistics, University of Copenhagen. John Wiley & Sons, Inc., New York, 1952. xii + 783 pp. Illustrated. 17 × 26 cm. $9.**

THE author presents in this text a thorough and conscientious treatment of fundamental statistical theory. Although the book is basically concerned with the mathematical development of the subject matter, it contains in addition a palatable blending of expository discussions and illustrative examples from various branches of engineering.

The text encompasses a considerable amount of material on a wide variety of statistical topics. Some of the standard topics include fundamental concepts of probability, properties of empirical and theoretical distributions, tests of significance, analysis of variance, and regression. Distributions of particular interest such as the normal, binomial, and Poisson distributions are treated in separate chapters. Noteworthy among the standard topics are the discussions of the power of a statistical test and confidence limits for a parameter, which first appear in connection with The Distribution of the Mean in Chapter IX.

The author has also included topics of considerable practical interest which are, nevertheless, seldom discussed in basic texts in theoretical statistics. The chapter on The Distribution of the Range can be cited as one example. In this chapter he discusses the control chart for the range and various test criteria commonly associated with the rejection of outlying observations. The chapter on Statistical Control is another example, in which the author gives a thorough discussion of the state of statistical control and the spheres of application of such methods as control chart techniques, tests based on runs, and a test based on the mean square successive difference. The fundamentals of sampling inspection (both by attributes and by variables) are also discussed at various places in the text, including a brief chapter on sequential sampling.

The overall purpose of the book is given in the final chapter, where the author states:

> ". . .the aim of this book is first and foremost to furnish the reader with simple and practical methods—which can be understood and applied by non-statisticians—for the handling of the majority of the problems which occur in everyday work."

This viewpoint is perhaps a trifle optimistic. The engineer with no previous knowledge of statistics would be hard pressed to browse through this book in its entirety. It is a mathematical text with engineering applications—not an engineering text.

However, when viewed in its proper light as a basic treatment of statistical theory, it is a well-rounded and thorough undertaking. The engineer should find it a reference text of considerable merit.

EDGAR P. KING

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WASHINGTON, D. C.

## ● POLAROGRAPHY. VOLUME II

***I. M. Kolthoff,*** **Professor and Head of Division of Analytical Chemistry, University of Minnesota, and *James J. Lingane,* Professor of Chemistry, Harvard University. Second edition. Interscience Publishers, Inc., New York, 1952. xvii + 568 (423–990) pp. Illustrated. 16 × 23.5 cm. $11.**

PUBLICATION of Volume II of "Polarography" completes the second edition of this well-known reference book.

In the preface to Volume II the author states, "The present volume II is concerned with practical applications in inorganic, organic, and biological chemistry, and with amperometric titrations." The presentation is similar to that given the same topics in the first edition. Inorganic substances are grouped to point up their chemical and polarographic similarities and differences, and organic compounds are grouped by classes, unsaturated hydrocarbons, carbonyl compounds, quinones, etc. The section on biological applications is concerned primarily with catalytic waves due to proteins and their degradation products, with the application of polarographic analysis to the diagnosis of cancer, and with the analysis of several vitamins and vitamin-like substances. The theory, techniques, and applications of amperometric titrations are presented in the last section of the volume.

Fortunately the authors have taken a broad view of what constitutes "practical applications." Their treatment of the individual elements and organic compounds gives half-wave potentials and diffusion current constants, many in condensed tabular form, for a wide variety of supporting electrolytes. Considerable discussion of chemical behavior as related to complex formation and reactions that may appear as interferences or aids to analysis are included. Polarograms have been reproduced to illustrate abnormal or nontypical current voltage curves. Information of this kind will appear as extremely "practical" to the analyst who may be deciding whether or not the polarographic method is suitable for a job at hand and must design a new set of procedures. An entire chapter is devoted to Analysis of Alloys and Technical Materials, in which procedures are given in sufficient detail to be used directly without further reference to the original literature. This chapter will appear as "practical" to the man working at the bench who is given the task of analyzing one of the many materials described.

The authors make a statement in the introduction to Volume I to which they refer in the preface of Volume II. They say: "Polarographic analysis is a complex subject that is far more simple on paper than in actual practice. The limiting current and other wave characteristics are influenced by a great many factors, and the effect of each of these must be recognized and controlled.

Anyone who attempts to apply polarography to a practical analytical problem without first taking the time to learn the fundamental theory of the method is simply inviting failure. No amount of elegant equipment can compensate for lack of fundamental knowledge. We do not mean to imply that routine polarographic analyses cannot be performed by technicians of limited training, but this should be done under the supervision of a chemist well versed in the theoretical and practical fundamentals of polarography." The two volumes of this second edition provide a complete and well-organized source of the theoretical and practical fundamentals of polarography which the authors would have all practitioners acquire. They will do much in making experts from novices and polarographers from experts.

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## • QUANTITATIVE ANALYSIS

***William Marshall MacNevin,*** **Professor of Analytical Chemistry, and** ***Thomas Richard Sweet,*** **Assistant Professor of Analytical Chemistry, both at the Ohio State University, Harper & Brothers, New York, 1952. ix + 247 pp. 55 figs. 13 tables. 14.5 × 22.5 cm. $3.75.**

THIS is a brief, simply written text in quantitative analysis which is designed for engineers, premedical, and prepharmacy students as well as chemistry majors. It is successful in presenting clearly and explicitly the necessary directions for a laboratory course in quantitative analysis together with a concise explanation of reasons for the procedures. It is expected that the instructor may wish to supplement the discussions of theory.

The laboratory experiments include, in addition to gravimetric determinations of sulfate, chloride, iron, nickel, and silica, and usual volumetric determinations, more specialized analyses, such as carbon dioxide in carbonates, carbon in steel, photometric determination of iron in alloys. Of especial interest is the determination of sulfate by ion exchange and a versenate determination of hardness in water. The early experiments, both in gravimetric and in volumetric work, are written with carefully detailed directions and seem suitable for students with meager chemical or mathematical background. Certain early difficulties such as weighing by sensitivity are omitted entirely and the calibration of weights is in the last chapter. Errors and significant figures are too briefly discussed. The authors have simplified laboratory instructional problems by including sample notebook pages, suggestions for securing samples and for grading reports.

The reviewer would not select the book for chemistry majors but feels it has much merit for those who wish a limited acquaintance with the field, or who wish to use it for a special purpose.

LUCY W. PICKETT

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## • TEXTBOOK OF QUANTITATIVE INORGANIC ANALYSIS

***I. M. Kolthoff*** **and** ***E. B. Sandell,*** **Professors of Analytical Chemistry, University of Minnesota. Third edition. The Macmillan Co., New York, 1952. xv + 759 pp. 15.5 × 23.5 cm. $6.50.**

Probably all teachers of analytical chemistry are familiar with the earlier editions of this comprehensive and authoritative text of quantitative analysis. Designed for use both in a beginning and advanced course by the serious student of chemistry, it is one of the most important books in the field.

The present edition varies from the second chiefly in an enlargement and reorganization of the chapter on physical methods of analysis giving more attention to such subjects as fluorescence and flame photometry. Another chapter involving extensive revision is that entitled Quantitative Separations, which gives fuller treatment to ion exchange and chromatography as well as the use of organic reagents. A discussion of the Brönsted theory is included in this edition although classical terminology is used in most of the text.

A number of new problems have been added and the increased size of page permits a more attractive and more easily read edition.

LUCY W. PICKETT

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## • REFERENCE BOOK OF INORGANIC CHEMISTRY

***Wendell M. Latimer,*** **and** ***Joel H. Hildebrand,*** **Professors of Chemistry, University of California. Third edition. The Macmillan Co., New York, 1951. xii + 625 pp. 50 figs. 124 tables. 14 × 21 cm. $5.**

THIS is the third edition of an excellent and very well-known reference book, which, although not a text in the ordinary sense, should find widespread use in supplementing most general and inorganic chemistry courses, particularly those of a more rigorous nature.

The present edition has the same form and, to a large extent, the same material as the previous editions. Altogether about 50 pages of new material have been added. At first glance most of the pages appear to be identical with those of the second edition but close examination reveals that many pages have been revised and brought up to date by the change of a word or number, revision of a sentence, or deletion of sentences and substitution of others for them. In some cases whole pages or sections have been rewritten and expanded. Chapter XXII, The Radioactive Elements, of the second edition has been rewritten and expanded into Chapter XXII, The Actinide Elements, and Chapter XXIII, Nuclear Reactions, of this edition. Many oxidation-reduction potential diagrams have been added. Tables have been revised and brought up to date. In the appendixes a new table of the abundances of the elements has been added.

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## • POLARIZED LIGHT IN METALLOGRAPHY

**Edited by** ***G. K. T. Conn*** **and** ***F. J. Bradshaw.*** **Academic Press, Inc., New York, 1952. xi + 130 pp. 31 figs. 22 plates. 4 tables. 14.5 × 22.5 cm. $3.80.**

THIS short text, which surveys the applications of polarized light in the examination of metals, alloys, and ores, is sponsored by the Optical Methods Sub-committee of the British Iron and Steel Research Association. The book comprises seven chapters written by eight experts but does not suffer from lack of continuity, although the various authors do not always agree in their points of view. The first two chapters, written by Conn and Naish, deal briefly with the pertinent optical principles involved in the production of polarized light and with its reflection and absorption by isotropic and anisotropic materials. The third chapter by Hallimond and Taylor considers critically microscopes and auxiliary equipment and also procedures for work with reflected polarized light. In chapter four by Perryman, which deals with the examination of metal surfaces for grain structure and identification of phases, numerous plates strikingly illustrate the possibilities of the polarized light method. Chapter five by Morrogh, which points out the possibilities of identification of inclusions in metals and alloys, also contains several highly informative plates. In the sixth chapter the use of reflected polarized light in the study of ores is considered by Cohen, and includes a number of interesting specific examples. The book concludes with a short summarizing chapter by Mott upon the significance of polarized light in the study of metals and ores.

The book is well documented and contains a glossary of optical terms. This small book presents a critical survey of the present status and possibilities of polarized light microscopy, stressing not only the advantages but also painstakingly considering possible pitfalls and limitations of the method. It is felt that the authors have performed a valuable service in carefully evaluating what should become an increasingly important branch of metallography. The book is recommended to all those interested in the microscopical examination of metals, alloys, and ores.

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## ● SEMIMICRO QUALITATIVE ANALYSIS

***Paul Arthur,*** **Professor of Chemistry, and** ***Otto M. Smith,*** **Professor Emeritus of Chemistry and Director of Research Foundation, both of Oklahoma Agricultural and Mechanical College. Third edition. McGraw-Hill Book Co., Inc., New York, 1952. xi + 285 pp. 27 figs. 8 tables. 15.5 × 23.5 cm. $4.**

SINCE semimicro qualitative analysis is the subject of almost as many texts as is general chemistry, it is difficult for a teacher to appreciate a new text unless it shows marked advantages over its fellows. Changing texts in qualitative analysis is a major operation inevitably involving some retooling of laboratory locker equipment and extensive change of reagent solutions. Hence, the teacher of analytical chemistry is inclined to look with something less than enthusiasm at "another qual. text." In this reviewer's opinion this text offers no particular advantage over many others in the field.

The theoretical portion of the text, comprising the first ten chapters, introduces the reader to physical-chemical principles of ionic equilibria. The theoretical material is developed more in accord with the needs of a physical chemistry course than with those of a qualitative analysis course. For example, the principle solubility product which is encountered very early in the laboratory is discussed in the text after the material on ionization of acids and bases and buffer calculation. In view of the physical chemical approach, it was surprising to find the mention of activity and activity coefficient limited to a footnote. Oxidation-reduction reactions are not considered until the tenth chapter where the ion-electron method for balancing is used but not explained. The chapter on complex ions is inadequate. The idea of maximum coordination is not developed and the chapter is without one mention of chelates although liberal use is made of organic reagents in the laboratory portion of the text. Illustrative of the lack of coordination of lecture and laboratory material we find the complex $HgI_4^{--}$ mentioned in the chapter on complex ions, but $HgCl_2$ in the laboratory portion. The text also suffers from a lack of chemical equations, especially those of the metals with the many organic reagents used and those of anion reactions generally.

The mistakes found include:

$Cu_2^{2+}$ should be $Cu^+$ (p. 132)
$Co(OH)_2 + NH_3$ yields $Co(NH_3)_6^{3+}$ not $Co(NH_3)_6^{2+}$ (p. 225)
Formula Ni dimethylglyoxime should indicate 4 Ni-N bonds rather than 2Ni-N and 2Ni-O bonds (p. 233)

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## ● SYNTHETIC METHODS OF ORGANIC CHEMISTRY. VOLUME 6

***W. Theilheimer.*** **Interscience Publishers, Inc., New York, 1952. xi + 387 pp. 16.5 × 23.5 cm. $12.90.**

THE sixth volume of this now familiar annual survey of organic reactions includes material taken from the literature of 1949 and 1950. As in the earlier volumes the information is presented in the form of short abstracts of experimental procedures. The reactions are arranged according to the elements which are to be bonded and according to the type of reaction (*i. e.*, addition, rearrangement, exchange, and elimination). A special symbolism is used for the reaction types; readers who master the simple rules for assigning a "reaction symbol" are able to locate reactions in the book without reference to terms such as the Beckman rearrangement, aldol condensation, or Malaprade reagent. However, a conventional index, listing "name" reactions, functional groups, general classes of compounds, reagents, etc., is provided for those who prefer not to make use of the "reactions symbols."

A specific illustration—for example, finding information on the conversion of the carbonyl group to methylene—will serve to describe the use of the cataloguing scheme, as well as the kind of information presented. First the reaction symbol, HC ⇵ O, referring to the formation of the carbon-hydrogen bond (HC) by exchange (⇵) with oxygen (O), is constructed. Then the page on which such processes are treated is located. This may be done directly or with the help of the table of symbols at the back of the book. At the proper place in the book we find abstracts of pertinent work on the Clemmensen reduction published in 1949 and 1950 by Leonard and by Clemo. Also we note references to the Wolff-Kishner method, and are reminded by a reference to Plattner (1949) and to others that the keto group attached to an aromatic system may be converted to methylene by catalytic hydrogenation. In this particular section, it would have been helpful to the searcher if a cross reference were provided to the two-stage process of transforming carbonyl to methylene, involving thioketal formation followed by Raney nickel desulfurization. This last method is found under HC ⇵ S.

The reader would be led to the same abstracts by looking in the conventional index for such entries as Clemmensen, Kishner, Wolff-Kishner, (Raney) nickel, zinc, etc.

Theilheimer's occasional failure to include Kekulé double bonds in the structural designation of aromatic systems is not the best practice and can lead to unnecessary ambiguity. Thus we find a structural formula on page 23, written without double bonds, which does not distinguish between a furan and a tetrahydrofuran derivative. Only after reading the abstract does it become clear that a furan compound is intended. However, this and other minor criticisms do not detract significantly from the value of the book. It may be predicted that this volume of synthetic methods will find its place with its earlier counterparts as a standard secondary source.

Parenthetically, it is interesting and gratifying to realize that a group of chemical industries is sponsoring the Theilheimer series. It has been pointed out before that substantial support by industry for other worthy publications, such as *Chemical Abstracts,* would be highly desirable.

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## ● SEAWEEDS AND THEIR USES

***V. J. Chapman,*** **Professor of Botany, Auckland University College. Pitman Publishing Corp., New York, 1952. xiv + 287 pp. 52 figs. 20 plates. 14.5 × 22 cm. $6.**

THE first of the nine chapters cover the occurrence and distribution of seaweeds. This is well covered in an interesting manner for the various sections of the globe with emphasis on the more important seaweeds and the zonation in the various regions. Sketches of a number of seaweeds are included.

Unfortunately, previous publications of which the author depended for information on the distribution of *Macrocystis pyrifera* along the Pacific Coast are mistaken as to the distribution of the species. The commercial stands of *Macrocystis pyifera* are found in a limited region along the California and

Baja California costs. The superficially similar *Macrocystis* found farther north is the noncommercial shallow water plant, *Macrocystis integrifolia*. The bulk of the *Nereocystis luetkeana* or "bull kelp," which predominates north of the *Macrocystis pyrifera* beds, is found in much shallower water than this and previous reports indicate. In fact, most of this "bull kelp" would have to be considered noncommercial since it grows in water too shallow and dangerous for barge harvesters.

Historical aspects of the kelp industry are thoroughly covered in the following three chapters. Potash, iodine, and fermentation are considered in detail. The author has performed a service in collecting much of this old literature in one place. However, this section must be mildly criticized for being written in a style that indicates that seaweed industries based on potash, iodine, and fermentation are still of current interest. It isn't until the last page that the author brings out that this entire section is of only historical interest for the forseeable future.

The agar industry is discussed in the fifth chapter with an initial coverage of the old Japanese agar industry. War time activities of the Western powers to develop agar industries independent of Japan are documented.

Food and fertilizer uses of seaweeds are treated in detail in the following two chapters. The literature attempting to show from protein and fat analyses that the brown algae compare with hay and oats in food value is reproduced. Many specialized human food products produced in the orient from various types of seaweed are described. Actually, very little success has accompanied the many attempts to use seaweed for their food value. Seaweed meals are used as animal food supplements mainly because of the trace elements and vitamins present. Again, this section is chiefly of historical value, serving to gather in one place literature on discontinued uses of seaweed as food. The interest in cultivating *Chlorella* and other green algae under specialzed conditions to produce high fat or protein contents has developed mainly since this book was written and is not included.

Chapter VIII on Algin and Seaweeds in Medicine and the Home is poorly organized and mistitled. The errors unknowingly quoted from the literature are too numerous to mention. In fact, less than two pages of the six devoted to algin uses include present commercial applications of algin.

In the last chapter on supplies of seaweeds, the various government sponsored surveys of seaweed resources are presented. The table on page 240 giving seaweed densities in the Pacific Coast beds is correctly quoted from the original, but the original report contained densities that were much too high.

A useful and extensive bibliography is found at the end of the book.

In summary, "Seaweeds and Their Uses" represents a worthwhile collection of historical data on discontinued products and uses for the seaweed industries. The section on distribution of seaweeds is valuable. However, this book fails to present a useful or accurate picture of the present seaweed industry. The coverage of the present algin industry is inadequate and inaccurate. The present important carregeenin industry is not covered adequately, being dismissed with a few scattered references.

WILLIAM H. MCNEELY

SAN DIEGO, CALIFORNIA

## ● CHEMISTRY OF THE METAL CHELATE COMPOUNDS

***Arthur E. Martell,*** **Professor of Chemistry, Clark University, and** ***Melvin Calvin,*** **Professor of Chemistry, University of California. Prentice-Hall, Inc., New York, 1952. xi + 613 pp. Illustrated. 16 × 24 cm. $13.50.**

THIS book is the outgrowth of some 10 or 15 years of research by the authors in the field of chelate compounds and represents the first attempt to bring together an extensive collection of useful data on the subject and to discuss the chemistry of metal chelate compounds. The authors state in the preface that "since these researches are to be found in almost every field of chemical activity, ranging from dyestuff chemistry through the very broad applications in analytical chemistry to the studies on the mechanism of enzyme action, it is to be expected that the book will appear as a different entity to each group of observers." The authors frankly state that no attempt was made to make a complete compilation of all the known chelate compounds or to list all their applications; rather, they "have tried to state the principles of the structure and behavior of metal chelate compounds in such a matter as to engender the creation of new compounds and new applications, as well as to contribute to an ultimate understanding of their mode of action in nature."

The main section (513 pages) of the book is divided into 10 chapters. An introductory chapter dealing with definition of terms, the importance of chelate compounds, the theory of their formation, etc., is followed by chapters with the following headings: Methods of Determining the Presence of Chelates, Stabilty Constants, Influence of Structure of the Chelating Agent, Effect of Metal Ion, Bond Type, Structure of Chelate Compounds, Catalytic Effects of Chelate Compounds, Separation of Metal Ions, and Uses of Chelating Agents. Then follow four useful appendexes on Chelate Stability Constants (48 pages) with references to the original literature, Optical Activity and Related Properties (7 pages), Glossary of Terms, and Thermodynamic Constants for Reactions of Metal with Chelating Agents. The book ends with author and subject indexes.

This book should have a wide appeal because of the extensive role metal chelates play in so many fields of interests. The authors are to be thanked for making readily available so much useful information on this subject, and for their lucid discussions. The book presents an up-to-date, critical and stimulating treatment of the subject; it is well documented with tables of data and references to the original literature. Structural formulas and figures are generously used throughout the text. Printing and binding are good. The book supplies a need by all those who are interested in the chemistry of the metal chelate compounds.

UNIVERSITY OF VIRGINIA JOHN H. YOE
CHARLOTTESVILLE, VIRGINIA

## ● THE TERPENES. VOLUME III

***Sir John Simonsen,*** **Director of Research, Colonial Products Research Council, and** ***D. H. R. Barton,*** **Reader in Organic Chemistry, Birkbeck College, University of London. (With Addenda to Volumes I and II by** ***Sir John Simonsen*** **and** ***L. N. Owen.*** **) Second edition. Cambridge University Press, New York, 1952. xi + 579 pp. 14.5 × 22 cm. $10.**

WITH the publication of Volume III the second edition of "The Terpenes" is complete. Volume I describing acyclic and monocyclic terpenes was published in 1947, Volume II, covering the dicyclic compounds, in 1949. Sesquiterpenes, diterpenes, and their derivatives are the subject of Volume III which also includes a 61-page addendum to the first two volumes. Thus the entire monograph is brought up to data through 1949 and some references to work published in 1950 are included.

The principal emphasis of these volumes is on the determination of the structures of the various terpenes or their derivatives and the treatment is both critical and authoritative. Reference is also made to the occurence, isolation, and purification of the compounds, but commercial importance and abundance are seldom indicated. Modern methods of structure determination, especially spectroscopic methods, and recent advances in the stereochemistry of these cyclic systems are covered, but a more extensive treatment of these subjects would have been welcome. Special attention is given to those compounds now under active investigation. The result is a work which is not only indispensable to the research chemist active in the terpene field, but of general interest to all students of organic chemistry for its exposition of structural determination methods.

A feature of these volumes is the abundance of structural

formulas, which are accurately and attractively executed. Both the format and printing are good, with only the rather awkward system of marking references by printer's signs instead of numbers to detract from the technical perfection in make-up. Sir John Simonsen and his collaborators (L. N. Owen for the first two volumes and D. H. R. Barton for the third) have made a fine contribution to the literature of organic chemistry in their revision of this great monograph.

THOMAS L. JACOBS

UNIVERSITY OF CALIFORNIA
LOS ANGELES, CALIFORNIA

## ● FUNDAMENTAL PRINCIPLES OF POLYMERIZATION

***G. F. D'Alelio,*** **Vice President and Manager of Research, Koppers Co., Inc., Pittsburgh. John Wiley & Sons, Inc., New York, 1952. x + 517 pp. Illustrated. 15.5 × 23.5 cm. $10.**

THE author has written an understandable book on a complex subject. In days gone by polymerized messes were dumped into the sink because they failed to crystallize. They still don't crystallize, but they are invaluable commercially, so that we are obliged to learn how to work with them. Statistical treatments are currently revealing much order where chaos once reigned. One will find here detailed information about the polymerization of many different systems under various circumstances. Molecular weight determinations from viscosity, sedimentation rate, and light scattering are all considered at length. The definition of terms and the discussion of the nature of high polymers are all good. This book is a careful effort to bring together in usable form a great deal of the information in the field and in this it is successful. The references are drawn from a wide field and provide a wealth of useful background material. One could wish the field itself was more systematic, but this is not the fault of the author.

HENRY EYRING

UNIVERSITY OF UTAH
SALT LAKE CITY, UTAH

## ● STYRENE: ITS POLYMERS, COPOLYMERS AND DERIVATIVES

**(American Chemical Society, Monograph Series) Edited by *Ray H. Boundy,* Director of Research, The Dow Chemical Co.; *Raymond F. Boyer,* Director, Physical Research Laboratory, The Dow Chemical Co.; and *Sylvia M. Stoesser,* Editorial Assistant. Reinhold Publishing Corp., New York, 1952. xxii + 1304 pp. Illustrated. 16 × 23.5 cm. $20.**

THIS is a joint effort by a group of chemists at Dow Chemical Company with some outside collaboration to cover completely the chemistry and physics of styrene and polystyrene. The subjects treated include the manufacture and properties of styrene, the polymerization of styrene, the molecular weight of polystyrene and the optical, electrical, mechanical properties and fabrication of polystyrene. Also included are chapters dealing with developments in Germany on the subject and a complete patent literature on styrene and polystyrene.

Practically all the literature on the subject is covered. The discussion is critical and many suggestions for further work in the field are put forth. The chapters on the molecular weight of polystyrene and on the degradation of polystyrene are very complete with regard to both theory and experimental data and much of the discussion is applicable to other polymers as well.

The editors are to be congratulated on their ability to unify such a wide variety of subjects. The book will be useful to chemists who want a complete and up-to-date treatment of the theoretical and practical aspects of the chemistry of polystyrene and styrene.

GERALD OSTER

POLYTECHNIC INSTITUTE OF BROOKLYN
BROOKLYN, NEW YORK

## ● INTRODUCTORY MYCOLOGY

***Constantine John Alexopoulos,*** **Professor of Botany and Plant Pathology, Michigan State College. Art work by Mrs. Sun Huang Sung. John Wiley & Sons, Inc., New York, 1952. xiii + 482 pp. 187 figs. 15.5 × 23.5 cm. $7.**

AS THE title implies, this is a text for the beginning student of mycology. What makes it particularly valuable is that throughout it remains essentially on the introductory level. This can be said of no other of the several excellent mycology texts which have appeared in recent years. Furthermore, there has been maintained throughout an easy, conversational style which because it smacks strongly of the author's personality and enthusiasm for his subject makes for easy and sustained reading.

After the usual introductory material, noteworthy for the care with which the author indicates the derivation of the words making up the special vocabulary of the science, the "phyla" of fungi are successively considered. These start with the *Schizomycophyta* and *Myxomycophyta* and continue with the *Eumycophyta,* which contains the classes of true fungi, namely, the *Phycomycetes, Ascomycetes,* form-class *Deuteromycetes* and *Basidiomycetes.* Series and subclasses are recognized under these larger categories.

Each class is introduced by a chapter dealing with general morphological features and life cycles and is followed by chapters dealing with the groups at the family level. Wherever appropriate, special features are interpolated, such as importance to man and diagrams of life cycles. Analytical keys to the orders are also included. Each chapter ends with a bibliography of papers, primarily those in English, pertinent to material considered in it. The book itself terminates with a glossary of terms, a list of acknowledgments of sources of the well drawn illustrations, and an index.

Alexopoulos' text can be recommended to the novice with the assurance that, for the most part, he will be able successfully to follow the author through the intricate maze of structural terms, life cycles, etc., with which the modern science of mycology is burdened.

FREDERICK K. SPARROW

UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN

## ● PROGRESS IN COSMIC RAY PHYSICS

***J. G. Wilson,*** **Lecturer, University of Manchester, Manchester, England. Interscience Publishers, Inc., New York, 1952. xvi + 557 pp. 164 figs. 85 tables. 15 × 23 cm. $12.**

AUTHORITATIVE and systematic treatises rarely appear in a field of science which is rapidly developing. Only when the principal phenomena are reasonably well understood and coordinated is it possible to prepare a systematic text. The great number of workers in the many phases of cosmic radiation are amassing more and more data without developing a corresponding clarification of the whole picture. There is a real need for attempts to systematize our knowledge in the many phases of this subject. This volume and the promised succeeding volumes will be of great assistance to the workers in the field. One does not find here a systematic presentation of the phenomena, but rather, surveys of the status of progress in special fields of the subject, prepared by those who have contributed to those special fields.

The contents of this volume includes: (1) a qualitative description of the radiation and elastic interaction of high-energy cosmic ray primaries in nuclear emulsion (Camarini, Lock, and Perkins); (2) the evidence for and the properties of unstable particles (Butler); (3) a survey of the problem of nuclear forces in terms of meson fields, with an attempt to make a consistent picture through the use of *pi, mu,* and heavy mesons (Michel); (4) an analysis of the part played by the heavy nuclei as primary cosmic ray particles and their influence on cosmic ray phenomena (Peters); (5) a report on geomagnetic effects covering the details of the author's own measurements (Neher); (6) a survey of

the problem of diffusion and equilibrium of the various components of the cosmic radiation in the atmosphere (Puppi and Dallaporta); (7) a report on the depth variation of cosmic rays underground and its interpretation in terms of our knowledge of *pi* and *mu* mesons (George); (8) a detailed survey of the periodic and nonperiodic variations in the intensity of the different cosmic ray components, especially with regard to solar and siderial time (Elliot).

In spite of the variety of authors and subjects covered, the editor has succeeded well in presenting in a single volume a coordinated picture of the present status of much of the cosmic ray research. The general subject and author index covering all the chapters will be of valuable assistance to the research worker in this field. The reports presented in this volume are excellent examples of the type of material that one would like to find more often in the Reviews of Modern Physics.

ROBERT B. BRODE

University of California
Berkeley, California

## ● ELIAS E. RIES, INVENTOR

***Estelle H. Ries.*** **Philosophical Library, Inc., New York, 1951. xii + 369 pp. 14 × 22 cm. $4.75.**

The story of Elias E. Ries as told by his daughter here is a human document of great significance to anyone concerned with American progress. It should appeal especially to inventors, engineers, and scientists and also to patent lawyers, and to those whose industries are built upon the inventions referred to in this story of a pioneering inventor who laid the groundwork for the inventions that made these industries possible in our modern world of electricity.

Today we hear so much about research laboratories, but here is a biography of a man who went it alone, and lost because of absurd patent regulations or abuse of them, because of human pettiness and conflict with patent lawyers. From more than 200 inventions not one brought him enough to even pay the debts contracted in its development. Today his name ranks with the great names who founded the great American electrical industries, and these amazing stories are revealed by his daughter. To mention only a few of these are his studies with talking pictures, of heating applied to railroad cars, electrical methods for manufacturing tools and machinery, a safety control for electric elevators that made modern skyscrapers possible, and his basic patents upon both direct and alternating current which made possible the invention and development of electric railways.

This biography is a crusading book in that the writer not only points out the hazards encountered by inventors but makes suggestions for improving these conditions and protecting the research of creative thinkers like her father.

GRETA OPPE

Ball High School
Galveston, Texas

## ● TABLES OF CHEMICAL KINETICS: HOMOGENEOUS REACTIONS

**Edited by *N. Thon.* Circular No. 510 of the National Bureau of Standards, 1951. xxiv + 731 pp. of tables. 23 × 29cm. For sale by the Superintendent of Documents, United States Government Printing Office, Washington 25, D. C. $4.**

This work is a cooperative effort of the National Bureau of Standards, The Committee on Tables of Constants of the National Research Council, and Princeton University. The data are on punched sheets bound in a paper cover. Subscribers will be sent supplementary sheets which may be inserted in their proper place by removing the cover and assembling the whole material in loose-leaf binders. Assisting the editor were P. G. Kelemen, G. Parravano, G. S. Forbes, M. Szwarc, and H. A. Taylor.

The purpose of the tables is to present an evaluated compilation of the numerical data on rates and rate constants of homogeneous chemical reactions. Only experimentally determined facts have been listed, since it is not the purpose of the volume to give interpretations and theory of the experiments. The reactions are given a code number and are classified under headings such as racemization, branching isomerization, esterification, ester exchange, condensation, hydrogen substitution, decomposition, association, and oxidation-reduction. The data given for the reactions vary, but in general they include the concentration range, medium or solvent, rate constant, energy of activation, temperature, frequency factor, and literature reference.

The book contains a remarkable assembly of valuable information on homogeneous reactions. As such it should be an excellent source of data for the teacher of physical chemistry and reaction kinetics.

ARTHUR A. VERNON

Northeastern University
Boston, Massachusetts

## ● CHEMICALS OF COMMERCE

***Foster D. Snell* and *Cornelia T. Snell,* Consulting Chemists. Second edition. D. Van Nostrand Co., New York, 1952. ix + 587 pp. 14.5 × 22 cm. $6.50.**

This book is said to have "all the principal facts about commercial chemicals from Abalyn to Zirconium Oxide," but the reviewer was never able to find Abalyn. There is no index to help out "This volume is designed to furnish information on the composition of actual commercial products as sold in commerce." It contains 38 chapters ranging from inorganic acids to vitamins, sterols, antibiotics, and hormones.

To one with chemical training the material given is quite elementary and often inadequate. To a nontechnical purchasing agent or salesman, this book might supply some useful information, although the nontechnical man might have difficulty in classifying the compound and locating the appropriate chapter.

KENNETH A. KOBE

University of Texas
Austin, Texas

## ● ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY, VOLUME IX: METAL SURFACE TREATMENT TO PENICILLIN

**Edited by *Raymond E. Kirk* and *Donald F. Othmer,* Professors and Heads, Departments of Chemistry and Chemical Engineering, respectively, at the Polytechnic Institute of Brooklyn. Assistant Editors, *Janet D. Scott* and *Anthony Standen.* The Interscience Encyclopedia, Inc., New York, 1952. xvi + 943 pp. Illustrated. 19 × 27 cm. Subscription price, $25. Single copy, $30.**

A count of the number of items which are referred back to previous volumes would be an interesting study of the ever-increasing coverage of the set of E.C.T.

The organic chemist scores heavily in this volume, with major sections devoted to naphthalene and derivatives, naphthenic acids, nitration, nitriles and isocyanides, nitro and nitroso compounds, nitrobenzene and nitrotoluene, nitroparaffins, nitrophenols, essential oils, onium compounds, organometallic compounds, oxalic acid, oximes, and particularly, organic analysis. The inorganic chemist will be interested in the elements molybdenum, nickel, nitrogen and oxygen and their compounds, nitric acid, nitrogen system of compounds, nucleonics, and ozone. The analytical chemist has microanalysis and microscopy. The physical chemist looks for the sections on molecular structure, osmosis and osmotic pressure, and oxidation-reduction. The biochemist has

important sections on microorganisms, nicotinic acid, nucleic acids, pantothenic acid, pectic substances, and penicillin.

The chemical engineer finds one unit operation, mixing and agitation, and one unit process, nitration (which overlooks the reviewer's work on process variables for nitration). He also is interested in nomographs, packaging, and packing materials. Technology scores with metal surface treatment, mica, mineral wool, molasses, nuts, paint, paper, paper coatings, methanol, and the oxo and oxyl processes.

Everyone will be interested in the general section on nomenclature and the lengthy section on nucleonics.

Although 1953 will not see the completion of the set of E.C.T., these nine volumes cover authoritatively so large a section of the literature of chemical technology that E.C.T. has become the first reference source to which a worker turns for information on a subject.

KENNETH A. KOBE

UNIVERSITY OF TEXAS
AUSTIN, TEXAS

## ● HANDBOOK OF CHEMISTRY

**Compiled and edited by *Norbert Adolph Lange*, registered professional engineer; assisted by *Gordon M. Forker*, General Electric Co., Cleveland, Ohio. Eighth edition. Handbook Publishers, Inc., Sandusky, Ohio. 1952. xvi + 1998 pp. 14 × 20.5 cm.**

THIS handbook has become part of the standard furniture in most chemical laboratories, and the eighth edition will prove to be even more useful than the preceding ones. Among the new subject matters in this edition are: a table of ionization potentials of elements; a classification of clay minerals; a glossary of inorganic nomenclature; a list of indicators and their properties; and a table of the density of moist air. Much of the rest of the subject matter has been rewritten and very little omitted.

## ● PAPER CHROMATOGRAPHY: A LABORATORY MANUAL

***Richard J. Block*, Department of Biochemistry, New York Medical College, New York, and Director, Biochemical Laboratories, The Borden Co., Yonkers, New York, and *Raymond LeStrange* and *Gunter Zweig*, Biochemical Laboratories, The Borden Co., Yonkers, New York. Academic Press, Inc., New York, 1952. x + 195 pp. Illustrated. 15.5 × 23.5 cm. $4.50.**

THE general nature of this field is well indicated by the fact that ten pages dispose of theory and the remaining 160 are devoted to general methods. Eight additional pages are entirely given over to bibliography. It is perhaps characteristic of the interests of the authors that the analytical methods are almost entirely devoted to organic materials with only a ten-page section on inorganic separations. This latter section, however, does not neglect the more recent use of electromigration. The book is well illustrated and includes two color prints of chromatograms of amino acids and inorganic substances, respectively.

## ● A GUIDE TO FILTER PAPER AND CELLULOSE POWDER CHROMATOGRAPHY

**Compiled by *J. N. Balston* and *B. E. Talbot*. Edited by *Tudor S. G. Jones*. H. Reeve Angel & Co., Ltd., New York, 1952. 145 pp. 10 figs. 15.5 × 23.5 cm. Paper bound. $1.50.**

A CONTRIBUTION to the practical technology to this new field of analysis. An excellent author's index helps to make this a useful bibliographic source for information in this field.

## ● ELECTROCHEMICAL DATA

***B. E. Conway*, The Chester Beatty Research Institute, London. Elsevier Publishing Co., Houston, Texas, 1952. xviii + 374 pp. 15.5 × 23.5 cm. $8.75.**

THIS work goes beyond the expectations implied in its title and includes much information on physical properties which, at first glance, would seem to be only remotely connected to electrochemistry. Literature references are pretty well up to date and a great deal of scattered information has been collected into a convenient reference. Some facts are extraordinarily well documented with bibliography.

## ● PRACTICAL CLINICAL CHEMISTRY. PARTS I, II, AND III

***Nell F. Hollinger*, Assistant Professor of Laboratory Practice, University of California, Berkeley, and *Richard K. Lansing*, *William J. Hayes*, *Dorothy L. Chandler*, and *Elizabeth B. Austin*, Associates in Public Health, University of California, Berkeley. The National Press, Millbrae, California, 1952. Part I, vii + 77 pp; Part II, 58 cards; Part III, 93 cards. Part I, 14.5 × 21.5 cm.; Parts II and III, 10.5 × 14 cm. $4.50 for set of three.**

PART I of this work deals with general principles involving the more conventional clinical determinations. Part II is printed on four by five and one-half inch cards, lightly bound together so that they can be separated and filed. These deal with "Notes on Methods," each card dealing with the routine detailing of someone's analytical method. Part III, "Solutions and Reagents" is similarly printed on cards, each giving the directions for preparing a solution or reagent.

This seems to be a unique type of publication which may be well adapted to the use of practical workers in this field.

## ● PROPERTIES OF THE PRINCIPAL FATS, FATTY OILS, WAXES, FATTY ACIDS AND THEIR SALTS

***M. P. Doss*, Technical and Research Division, The Texas Co., New York. Published by The Texas Co., New York, 1952. iii + 244 pp. 22.5 × 28.5 cm.**

EXTENSIVE tables arranged for convenient use.

# NEWS

## Side Glances in Science

In this column we are presenting a list of outstanding books in various fields of science. These books might not ordinarily be brought to the attention of chemists as none of them deal specifically with chemical subjects. We feel, however, that the outstanding merits of these volumes as contributions to knowledge in related fields, warrant the reading interest of all men of science.

*Soil Microbiology* by Nobel Prize Winner, Selman A. Waksman, Rutgers University. "A well-written exposition which presents its subject directly and simply."—*Chemical and Engineering News*. 1952. 356 pages. $6.00.

*Design for a Brain* by W. Ross Ashby, Barnwood House Psychiatric Hospital, Gloucester, England. ". . . the most original new step which has been taken in Cybernetics as a science."—Professor Norbert Wiener, Massachusetts Institute of Technology. 1952. 260 pages. $6.00.

*The Organization of Behavior: A Neuropsychological Theory* by D. O. Hebb, McGill University. ". . . the most important contribution to psychological theory in recent years."—Fred Attneave in the *American Journal of Psychology*. 1949. 335 pages. $4.50.

*High Speed Photography* by George A. Jones, F.R.P.S. Covers photography from its earliest beginnings to the most modern techniques and practices. 1952. 311 pages. $6.50.

*Color in Business, Science and Industry* by Deane B. Judd, National Bureau of Standards. "This definitive dissertation on color is . . . technically quite accurate . . .clear. . .well organized."—*American Scientist*. 1952. 401 pages. $6.50.

*Statistical Theory with Engineering Applications* by A. Hald, University of Copenhagen. ". . . a competent and conscientious first book on statistics."—*The Scientific Monthly*. 1952. 783 pages. $9.00.

*Understanding Heredity* by Richard B. Goldschmidt, University of California. A short and easily readable survey of basic genetics, called, by Professor A. H. Hersh of Western Reserve University, "the simplest yet most complete account . . . published." 1952. 228 pages. $3.75.

*Europe* by Samuel van Valkenburg, Clark University, and Colbert C. Held, University of Nebraska. A careful look at the continent, its geography and problems. ". . . well worth waiting for. . ."—Professor Trevor Lloyd, Dartmouth College. 1952. 826 pages. $7.50.

*The Development of Economic Thought: Great Economists in Perspective* edited by Henry William Spiegel, Catholic University of America. "Spiegel bids his readers address themselves directly to the thinking of economists ranging from Aristotle to Colin Clark. . ."—*The Scientific Monthly*. 1952. 811 pages. $6.50.


WILEY BOOKS

*They say . . . .*

**about Audrieth and Kleinberg's *NON-AQUEOUS SOLVENTS* (1953. 284 pages. $6.75).**

That it's a splendid "missionary effort" to acquaint chemists and engineers with the possibilities of non-aqueous systems. "It is a fine book and fills an important gap in chemical literature."—*Professor Joel H. Hildebrand, University of California.* "Those of us who have been teaching courses on non-aqueous solvents can now rejoice that a textbook is finally available."—*Professor W. Conrad Fernelius, The Pennsylvania State College.*

**about Therald Moeller's *INORGANIC CHEMISTRY: An Advanced Textbook* (1952. 966 pages. $10.00)**

That it strikes a sensible balance between the theoretical and descriptive approaches. ". . . very close to what I have considered should be covered in a modern course in Advanced Inorganic Chemistry. . ." says *Professor Leonora N. Bilger, University of Hawaii. Roy E. Thoma of the Oak Ridge National Laboratory* adds, "It is rare that such clear cut and definite prose appears in text material . . . as regards organization the text is ideally suited to either a one or two semester course."

**about D. W. Woolley's *A STUDY OF ANTIMETABOLITES* (1952. 269 pages. $5.00)**

*Journal of the American Chemical Society:* "It cannot fail to be useful to anyone interested specifically in antimetabolites whether as a reference for the experienced investigator or as a comprehensive survey to introduce a new student to the subject. . . . The book is so well rounded and covers the subject matter in such a way that it could well serve as a text for seminars, lectures or laboratory courses in undergraduate or graduate instruction."

**about Faith, Keyes, and Clark's *INDUSTRIAL CHEMICALS* (1950. 652 pages. $8.00)**

That its compilation of scientific, technical, and economic data on 106 important chemical substances makes it an ideal work, both as a reference and as an aid in showing students the economic aspects of chemistry in industry. *Professor Robert C. Elderfield of Columbia University* says, "The book fulfills a long felt want on the part of people working in so-called pure organic chemistry as to industrial practices which are followed."

**about Dallas T. Hurd's *AN INTRODUCTION TO THE CHEMISTRY OF THE HYDRIDES* (1952. 231 pages. $5.50)**

That between the covers of this timely new book is the first comprehensive, critical description of hydrides and the related hydrogen compounds. The book has been described as "cutting across most of the fields of chemistry, including inorganic, organic, physical, biological and analytical chemistry."

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Here's another great new laboratory expediter—Kemflex Polyethylene Tubing. Combining all of the fine features of Polyethylene, Kemflex tubing will withstand flexing almost indefinitely and can be used with any solution without fear of contamination. Order Kemflex tubing today and you'll find that it is the answer to your laboratory tubing needs.

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Forehead operation leaves hands free to open eyelids so water can be directed wherever chemicals might be lodged. Sanitary white baked enamel bowl is resistant to most fumes.

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The B & A Shower is the quickest and most satisfactory way to saturate a worker with gallons of water the instant an accident occurs, to prevent a disfiguring burn—even a fatality.

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THIS HAPPENS WHEN UNPROTECTED GLASS BOTTLES ARE BUMPED

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are widely used for the safe handling of glass bottles containing harmful chemicals; also the storage and recovery of expensive serums, biologicals, and other costly products.

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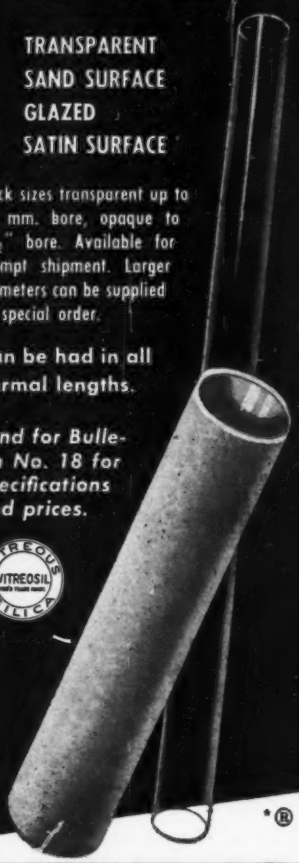

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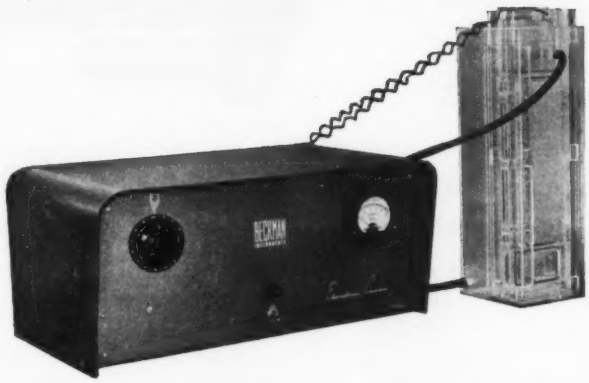

## The Beckman Electrophoresis-Convection Apparatus

Biochemists will find the new Beckman Electrophoresis-Convection Apparatus an indispensible tool—capable of fractionating mixtures of proteins possessing similar physical and chemical properties, heretofore unfractionable by previous methods.

Uses of the Beckman Electrophoresis-Convection Apparatus include such widely divergent determinations as:

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***The Beckman Electrophoresis-Convection Apparatus consists of four units . . .***

**1. Fractionation Cell where separation occurs into upper and lower reservoirs . . . 2. Two Platinum Electrodes which create a horizontal electrical field to aid separation . . . 3. Buffer Container, housing the fractionation cell and electrodes, designed to permit buffer solution circulation . . . 4. Control Unit containing 110 v. AC power pack and buffer circulation pump.**

*The high resolving power, volume fractionation, purity of separation and versatility of this equipment—plus ease of manipulation—save many valuable hours during preparation procedures.*

***For additional information on this new Beckman time-saver, write for Data File 91-36***

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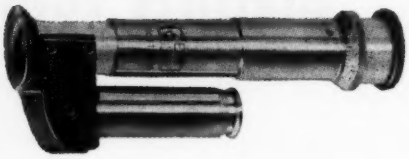

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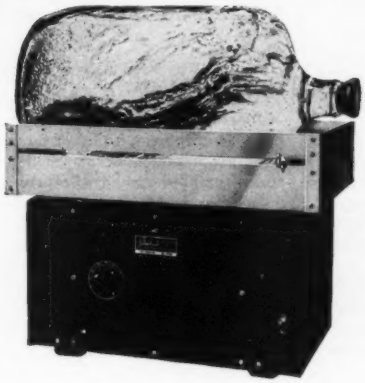

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# Out of the Editor's Basket

### Mallinckrodt Announces New Stormor Bottle

The Mallinckrodt Chemical Works has converted its entire one-pound and one-quarter-pound line of dry Analytical Reagents from round to more efficient, space-conserving, flat-sided bottles. Five of the new Stormor bottles can be fitted into the same space occupied by four equivalent volume round bottles. In addition to its space-saving advantage, the new package is easier to handle and open—its flat sides offer a much surer grip.

Also in new dress, and carried on the new bottles, is the familiar Mallinckrodt label which has been redesigned to increase even further its legibility and ease of spot selection from a line of bottles.

### New Midget Utility Pump

A new low-cost utility Model "MU" midget centrifugal pump for handling liquids where capacity requirements range from 0 to 6 gallons per minute from free flow to 6 feet of head has been added to its line of over 400 models of standard centrifugal and positive displacement pumps by Pioneer Pump Div. of Detroit Harvester Co., 19657 John R St., Detroit 3, Michigan.

Design and performance characteristics of the new pump make it readily adaptable to many diversified applications such as liquid circulation in agitation tanks, laboratory work, water cooling units, aquariums, and many others.

The Model "MU" is designed for continuous or intermittent operation. The pump is direct-connected to motor and requires minimum maintenance. This pump can be supplied in a wide variety of materials such as brass, stainless steel and Monel metal.

### Fluorescent Chemicals for Scintillation Counting

A series of high-purity fluorescent chemicals, useful in the field of scintillation counting, is currently being offered by Pilot Chemicals, Inc., of Waltham, Massachusetts. Some of these fluors are used in solution, others are incorporated in plastics, and others can be grown into large single crystals.

Among the materials being offered are Diphenylhexatriene, Tetraphenylbutadiene, and Quaterphenyl.

### Quartz Helix Balances

Now available are helix balances made of quartz fiber. Balances and pyrex glass cases are available to the microanalyst, biologist, or physical chemist in many designs for all types of microweighings. The manufacturer, Microchemical Specialties Company, describes quartz as the most nearly ideal material for small-scale weighing devices. Quartz helices extend to full length without hysteresis. They operate in any gas mixture or in a vacuum at any temperature. Expansion is negligible at all ordinary temperatures. Rapid microchemical weighing, either approximate or precise, is accomplished while preserving sterility of material studied.

Further information on the specific properties of quartz helices and other micro and ultramicro balances is available from the manufacturer, Microchemical Specialties Co., 1834 University Ave., Berkeley 3, California.

### New All-Purpose Black Light Inspection Unit

A new, high-intensity, long wave Mineralight designed for use as a portable black light inspection lamp in scientific laboratories, and for industrial and agricultural inspection, has been announced by Ultra-Violet Products, Inc., of 145 Pasadena Ave., South Pasadena, California.

This Model B-50-H Mineralight is an intense 100-watt long wave ultra-violet hand lamp operating on 110-volt a.-c. current. Throws a powerful directional beam of long wave (3660 Å.) ultra-violet up to 30 feet away. Will clamp rigidly


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new plastic laboratory tubing based on polyethylene resins

OFFERS THESE OUTSTANDING ADVANTAGES:

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1200

to its nontip base (containing transformer) and may be permanently locked to any desired position. Unit has easy-to-grip plastic handle, heavy 3-conductor primary and secondary cords, and is specially designed to burn cooler, assuring longer bulb life. Radiation is absolutely noninjurious, harmless to eyes or skin.

The new Mineralight Model B-50-H is made of light-weight, high-tensile-strength spun metal, finished in gray hammertone baked enamel. The matching hood and base fully enclose bulb and transformer. Both bulb and filter are safely recessed in the hood, and the switch is conveniently located at the base of the lamp.

**Eastman $C^{13}$ Isotope Concentrates Available at Lower Prices**

Sharp reduction in the prices of Eastman Isotope Concentrates of stable $C^{13}$ have just been announced by the Eastman Organic Chemicals Department of Distillation Products Industries, Rochester 3, New York.

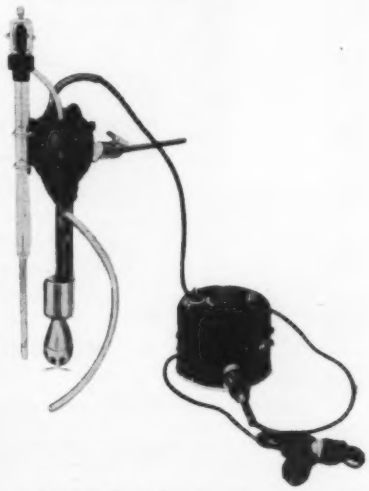
The price reductions apply to $C^{13}$-enriched barium carbonate, potassium cyanide, methyl alcohol, and methyl iodide. Hereafter they will be offered only in 60 to 70 atom per cent excess $C^{13}$. The natural abundance of $C^{13}$ is 1.1 atom per cent.

A non-radioactive isotope, $C^{13}$ is used in tracer studies of human metabolism and in other research where radiation safety precautions are impractical, the company stated. The customary method of detection is mass spectrography.

**Unique Constant Temperature Circulator**

The "Bronwill" Constant Temperature Circulator incorporates in a single unit, a stirrer with speed adjustment, 700-watt heater, temperature control with electronic relay, and an accurate thermometer.

It attaches by a pivoted extension rod to any support rod by means of a conventional clamp holder, adjusts to any position and, when inserted in any suitable glass or metal container, provides a compact, portable, water or oil bath adjustable to any temperature from room to 100°C. Temperature constancy of ± 0.01°C. can be achieved without difficulty in suitably insulated baths.



Additionally, this unit serves as a circulating system to circulate liquid of accurately controlled temperature through refractometers, polarimeters, spectrophotometers, viscosimeters, etc. At bath level it circulates up to 3 gallons of tempered liquid per minute. With water it has a discharge head of 6 feet. Heater, stirrer and contact thermometer together displace only about 100 ml. and weigh only 4 pounds. Total height, 20 inches.

Additional data may be had from Bronwill Scientific, Inc., 40 Worth St., New York 13, New York.

**New Ink Goes on Smooth Plastic Film**

Electrochemical Laboratories, Tulsa, Oklahoma, has introduced a new carbon ink of very unusual qualities. The carbon suspension has the covering powder of india drawing ink, but is so stable that it can be used in some fountain pens and withstands freezing and thawing without harm. Good adhesion on glass, smooth cellulose acetate, cellulose nitrate, methacrylate, and numerous water-repellant smooth plastic surfaces is claimed. Tests made by the firm show strong wear and heat stability, and indicate that the ink trace is not flaked by repeatedly rolling the film. It is a two-minute drying ink. Work done with this ink can be rendered water resistant by a brief heat cure at 180°F. The manufacturer advises that transparent colors suitable for projection are under development, and will be available soon. Though primarily designed for smooth plastics, the new black ink is also recommended for general purpose drawing, in which its nonclogging quality is a great advantage.

**Inexpensive Hand Polariscope**

The Pacific Transducer Corp., 11921 West Pico Blvd., Los Angeles 64, Cali-

TYGOTHENE is a "special application" laboratory tubing developed to meet the need for a semi-flexible tubing combining *solvent resistance* with maximum resistance to both acids and alkalies.

TYGOTHENE is a modified polyethylene. It possesses excellent resistance to aromatic hydrocarbons, ketones and esters up to an approximate maximum temperature of 160° F., but this varies with different solvents. Its resistance to strong mineral acids is superior to other tubings. TYGOTHENE is completely non-toxic, tasteless and odorless.

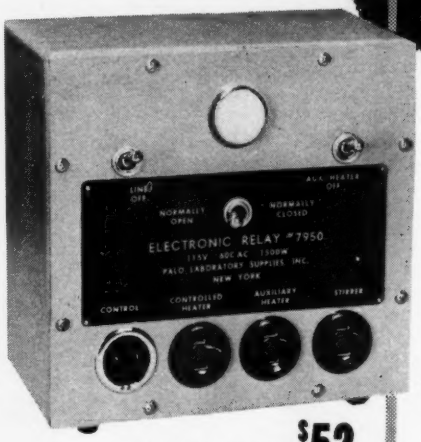
TYGOTHENE is made in two degrees of flexibility. Formulation "A" Tubing is of medium flexibility, while formulation "B" possesses the maximum flexibility possible with polyethylene compounds.

The natural color of the tubing is a translucent white, with translucency lessening as wall thickness increases.

TYGOTHENE is currently available in the most popular laboratory sizes either from your local laboratory supply house, or by writing direct to The U.S. Stoneware Co., Akron 9, Ohio.

MANUFACTURED BY THE MAKERS OF FLEXIBLE PLASTIC **TYGON TUBING**

# the *Palo* ELECTRONIC RELAY

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**Maximum Sensitivity by means of a Control Current . . . 0.5 Microamps**

The unit, encased in a gray Hammertone finished housing, is a versatile and self-contained product of electronic research and practical design. Everything is at the user's fingertips — no special inner connections to make.

### OTHER FEATURES:

- Extra outlets for stirrer and auxiliary heater
- Extra switch for auxiliary heater
- Switch for normally open or normally closed operation
- Load current 15 amps.—for 110 volt—60 cycles
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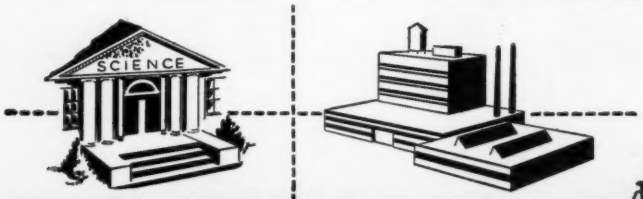


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fornia, announces a new hand polariscope for use in the laboratory and factory for the detection of strains in glass and plastics.

In the laboratory the instrument affords a ready means of checking for strains in chemical glassware and for the determination of the axes in crystal formations. In industry it can also be used for the detection of strains in clear plastics and in glass to metal seals.

The Model 242.3 Hand Polariscope is made with an oxidized non-rusting metal frame. The polarizer is fixed in one end of the frame. The analyzer is rotatable through 180° in the other end of the frame. There is a $3^1/_4$-in. space between ends for the object under examination. Any source of moderate intensity light is sufficient for the detection of strains in glass and clear plastic, and the quick inspection of glass molds and seals. The filters are made of 3-in. scratch-resistant Polaroid.

### Nozzle and Wheel Atomization in Spray Drying Equipment

As the result of recent developments in the new Bowen Test Laboratories, Bowen spray dryers are now offered using nozzle atomization. This is in addition to its present line with its wide range of centrifugal atomizers.

Because of the unique design of Bowen equipment it is possible to have the two different types of atomization interchangeable in the same spray drying installation. This makes for much greater flexibility of operation and allows the equipment to be used for a number of different products with widely varying characteristics.

The selection of the proper type of atomization can be accurately determined by tests in the Bowen Laboratories where the facilities have been increased to provide both nozzle and centrifugal atomization during the test of any single product. Texts can be run on full scale equipment and will provide an accurate basis not only of judging the relative merits of the two types of atomization, but will also furnish product samples and design data.

An illustrated booklet describing the Bowen laboratory may be had by request to Bowen Engineering Inc., North Branch 20, New Jersey.

### New Literature

● A brochure explaining the application of rectifiers to various operations has just been made available by the American Rectifier Corporation. The company has taken note of questions most frequently asked and has now compiled them, with their replies, in an interesting question-and-answer folder that reveals the many benefits of keeping d.-c. equipment working on a.-c. while retaining d.-c. speed control. Requests for the free brochure should be addressed to American Rectifier Corp., 95 Lafayette St., New York 13, New York.

● Schaar & Company offers a 16-page catalog of apparatus and equipment, featuring a complete listing of Paper Partition Chromatography equipment. Also included are many other newly introduced instruments and equipment for research, development, and control laboratories. Available on request from Schaar & Co., 754 W. Lexington St., Chicago 7, Illinois.

● A new bulletin describing the complete line of General Radio Equipment for measurements at ultra-high frequencies has just been published. Copies of the bulletin are available from General Radio Co., 275 Massachusetts Ave., Cambridge 38, Massachusetts.

● A new bulletin *Four Tools for the Laboratory and Pilot Plant* is available from Brosites Machine Company, Inc., 50 Church St., New York 7, New York. It illustrates and describes the Brosites Proportioning Pumps, the Web Cell Continuous Dialyser, and the Desaga Blender and Shaker.

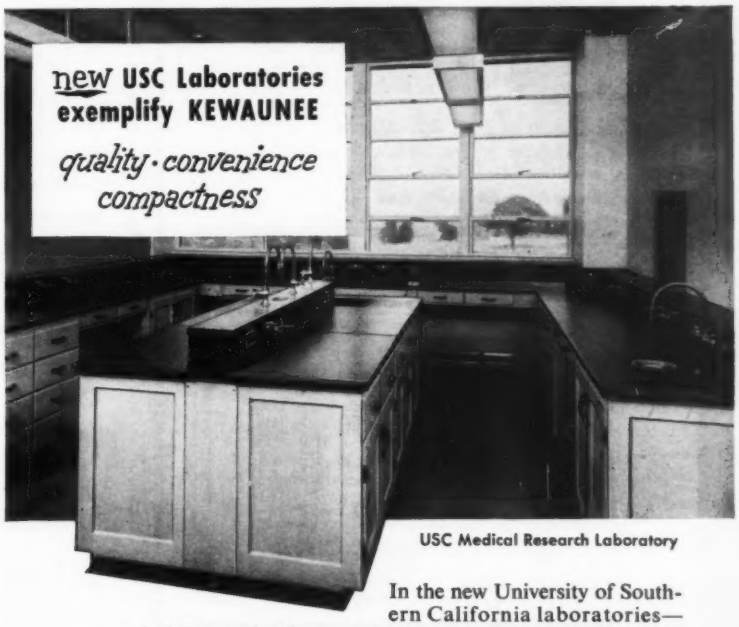
● Photovolt Corp., 95 Madison Ave., New York 16, New York., has just released their *Bulletin Number 800*, which describes the Photoelectric Densitometer Model 525. This instrument is designed for the evaluation of filter paper strips and charts as obtained by partition chromatography and paper electrophoresis.

● A new four-page illustrated bulletin presents Burrell reagents and auxiliary solutions for gas analysts.

Spotlighted and described are: "Cosorbent" for determinations of Carbon Monoxide by absorption; "Lusorbent" for illuminants; "Oxsorbent" for Oxygen; "Disorbent" for Carbon Dioxide and Burrell Sorbents "A," "B," "C," and "D," for specified unsaturated hydrocarbons.

A handy ordering chart lists catalog numbers, names of solutions, their uses, sizes available, and current prices.

Copies are available from: Burrell Corp. 2223 Fifth Ave., Pittsburgh 19, Pennsylvania.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USC Organic Chemistry Laboratory

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Does away with breakage ... mouthpieces ... rubber bulbs. Withstands flexing indefinitely. Durable and convenient. Smaller sizes used with short, straight discharge tube are perfect for washing of glass electrodes.

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| Capacity | 30 | 60 | 125 | 250 | 500 |
| Price | 1.15 | 1.20 | 1.30 | 1.60 | 1.85 |

*Discount of 10% on orders of dozen or more*

*Polyethylene "Police Rods"*

**FOR ALL STIRRING**

One piece molded, flexible, chemically inert polyethylene rods are unbreakable, can be bent to angle required. Thin paddle ends may be trimmed with scissors. Usable for short periods at temperatures up to 100°C. Wire stiffened.

| Catalog No. | Approximate overall length | Price, dozen |
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*Discount of 10% on gross lots*

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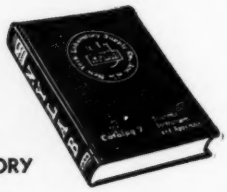

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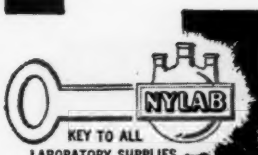


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In this beginner's text the traditional sequence of topics has been reshuffled in order to present a coherent view of the structure and behavior of matter in an easier and more logical way. Proceeding consistently from experiment to theory, from the familiar and the concrete to the unfamiliar and abstract, the student is given a solid basis for each successive step. An unusual number of graphical presentations.

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### PORTER AND STEWART

A one-semester course designed for students who need a brief but thorough introduction to organic chemistry as a basis for other courses, and for students in the general curricula of the arts and sciences. Current terminology is used and new topics are introduced in an elementary form.

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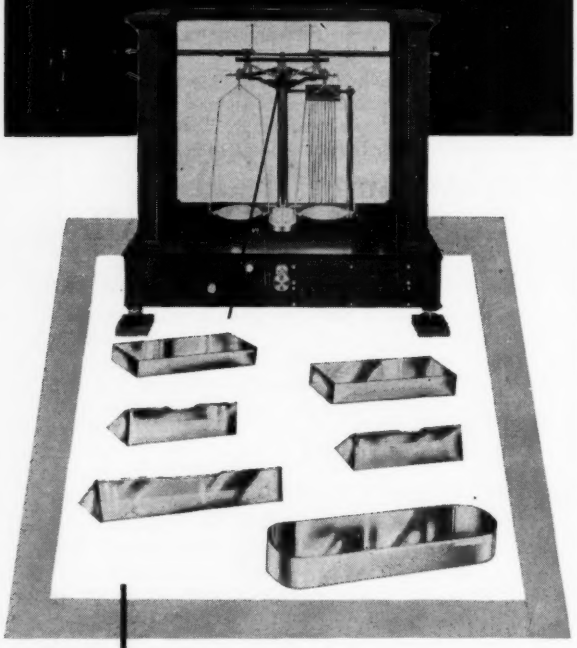

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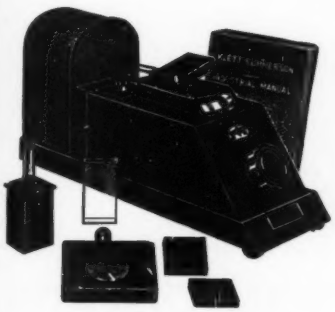

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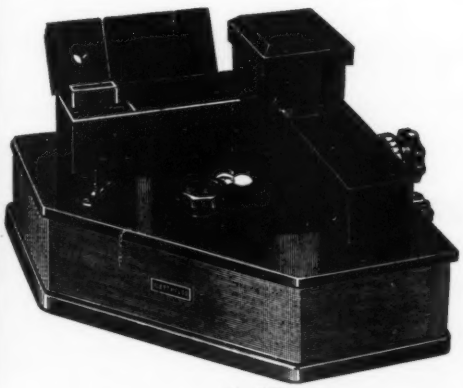

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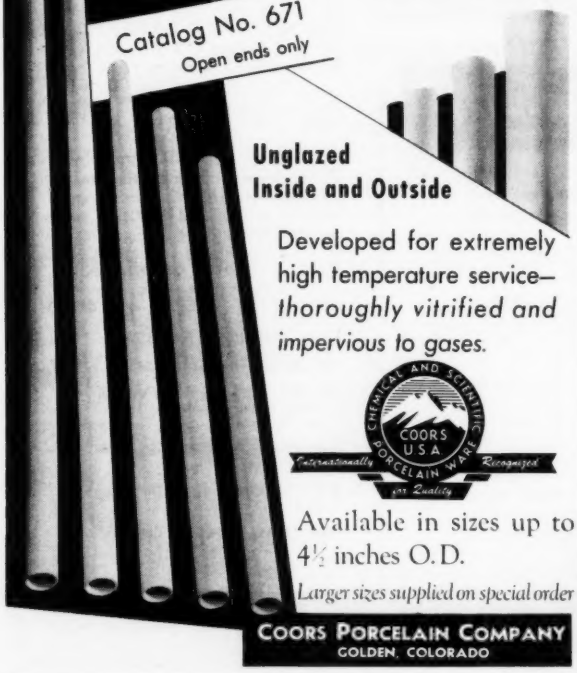

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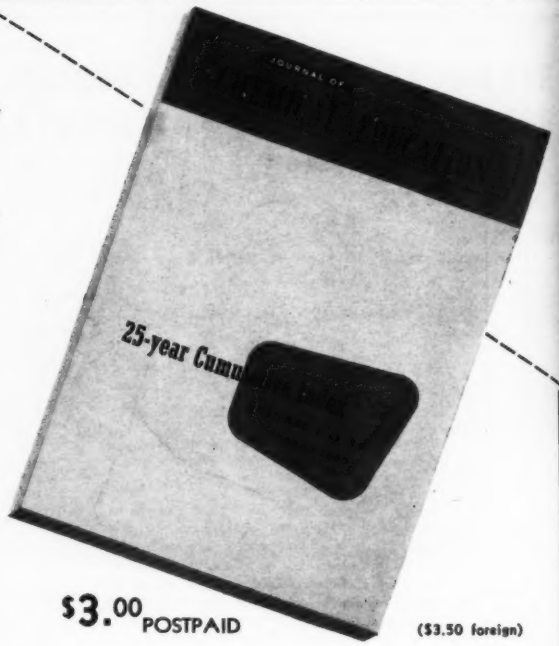


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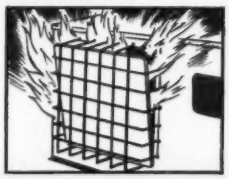

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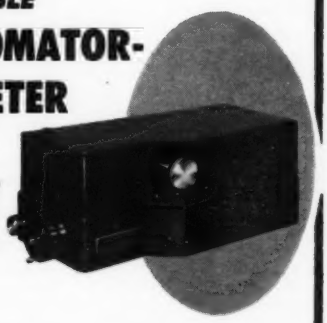
A DOUBLE MONOCHROMATOR-SPECTROMETER for the ULTRAVIOLET VISIBLE AND INFRARED RANGES



The optical system of the Farrand Double Monochromator has been designed to reduce scattered radiations to a negligible magnitude, to attain highest spectral purity, to isolate narrow wave lengths and to obtain optimum resolution. By simply interchanging prisms, the instrument may be operated at any chosen spectral region within the range of 0.2 to 35 microns.

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WILL **Laboratory Equipment**

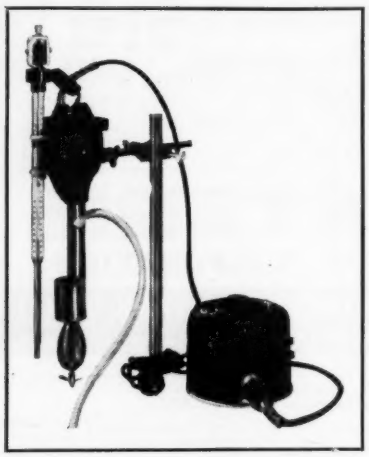
# NEWS OF THE MONTH

## New "BRONWILL"*

## CONSTANT TEMPERATURE CIRCULATOR

Pat. Pending

**instantly makes any suitable container a constant temperature bath or circulating system**



**28248T...For 115V 50-60cy AC...$210.00**

Here—in *one* compact unit—are all the components you need for a portable, accurate water or oil bath—and easily controlled circulating system for use with other instruments.

The new "Bronwill" Constant Temperature Circulator incorporates:

**Stirrer-circulator with speed adjustment**
**Contact thermometer**
**Immersion heater**
**Electronic relay**

The unit mounts outside the bath to eliminate vibration of bath or contents. It displaces only 100 ml. in the bath.

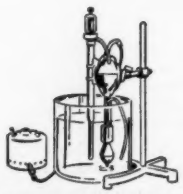
It circulates up to 3 gallons per minute of tempered liquid at bath level. With water, it has a discharge head of 6 feet.

Bath temperature is adjustable from room to 100°C, with sensitivity of 0.01°C.

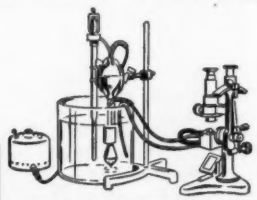
Complete with stirring and circulating unit, 700-watt heater, contact thermometer and electronic relay.

*Write today for descriptive literature.*

**Make these set-ups easily, rapidly**



**Constant temperature bath . . .** "Bronwill" Circulator attaches to any support rod with conventional clamp holder, and adjusts to any position. It stirs and circulates bath liquid at controlled speed. Adjusts to any temperature within its range.



**Liquid circulating system . . .** Circulates water of constant controlled temperature to refractometers, viscosimeters, polarimeters, spectrophotometers, other baths and vessels. Capacity, up to 3 gallons per minute.

**General temperature control . . .** Contact thermometer and electronic relay may be used together for highly sensitive control of incubating chambers, etc. Or relay alone may be used for many other purposes, on either normally-open or normally-closed circuit.

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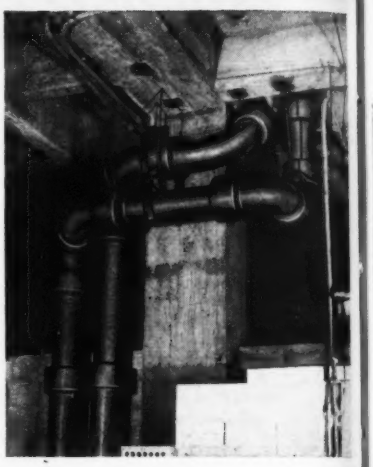
KNIGHT-WARE CHEMICAL EQUIPMENT

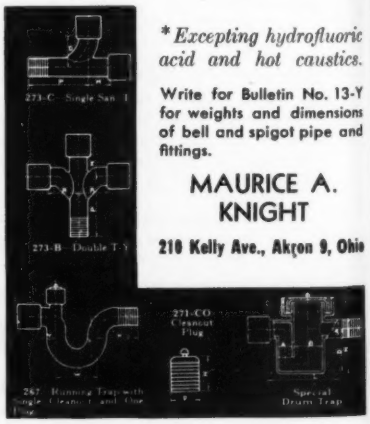


## The Pipe You Need for Corrosive Service

Knight-Ware acid proof pipe and fittings may be used wherever corrosive liquids and gases must be handled. This quality chemical stoneware is not just surface resistant but is physically tough and corrosion proof throughout its entire body. It is resistant to all acids and alkalies, hot or cold, in any concentration.*

In difficult installations special pieces may be required. These can be made of Knight-Ware at relatively low cost because no expensive molds are required in their manufacture. Knight-Ware is available in a variety of standard fittings and can be installed by any competent plumber.

Knight-Ware has found wide application for more than 40 years in the chemical processing industries, industrial laboratories, pharmaceutical plants, schools, newspaper engraving plants and medical centers.


273-C Single San. T
273-B Double T-Y
271-CO Cleanout Plug
267 Running Trap with Single Cleanout and One Vent
Special Drum Trap

** Excepting hydrofluoric acid and hot caustics.*

Write for Bulletin No. 13-Y for weights and dimensions of bell and spigot pipe and fittings.

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*and wider temperature range*

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**CONSTANT-TEMPERATURE BATH**

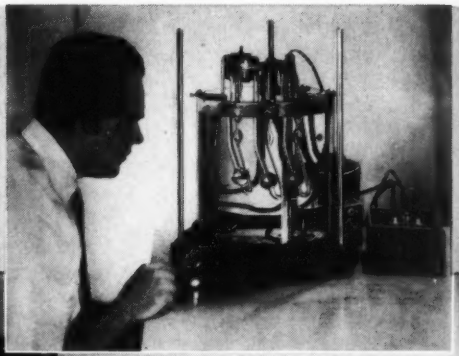
A Unitized Bath is a made-to-fit assembly which can be adapted to almost any type of constant-temperature work which can be carried out on a laboratory scale over the range between 20° and 200° C. and within an accuracy of 0.01° C.

The versatility of the Unitized Constant-Temperature Bath is the result of the ease with which different capacity jars, heaters, stirrers, thermoregulators and other necessary units can be combined to serve the exact needs of a particular laboratory requirement.

There are three sizes of bath jars with a capacity ranging to nearly eleven gallons. Close temperature control is assured by a choice of eight electrical heaters and three cooling coils, combined with three sizes of mechanical stirrers. These may be combined with any of four types of thermoregulator and any of Fisher's many different thermometers. Convenient voltage control unit enables user to change the output of any of his heaters. All Unitized Bath Units are easily assembled and interchanged.

**The Unitized Bath provides an ideal temperature control for viscosity, solubility, specific gravity and other fundamental measurements.**

**A special Unitized Bath assembly is available for the ASTM oil foaming test.**



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